

XIII. *An Account of Experiments made by Mr. John M<sup>c</sup> Nab, at Henley House, Hudfon's Bay, relating to freezing Mixtures. By Henry Cavendish, Esq. F. R. S. and A. S.*

Read February 23, 1786.

IN my observations on Mr. HUTCHINS's Experiments, printed in the LXXIII<sup>d</sup> volume of the Philosophical Transactions, I gave my opinion concerning the cause of the cold produced by mixing snow with different liquors. As there were some circumstances, however, which seemed to form a difficulty in the way of this opinion, I was desirous of having further experiments made on the subject; and at the same time I thought that, by proper management, a greater degree of cold might be produced than had hitherto been done. On mentioning the experiments I wished to have made to Mr. HUTCHINS, he very obligingly desired Mr. M<sup>c</sup> NAB, Master at Henley-House, to try them; who was so good as to undertake the business, and has executed it in the most satisfactory manner; as he has not only taken great pains, but has shewn the utmost attention and accuracy, in observing and relating all the phænomena which occurred, and has manifested great judgement in frequently adapting the manner of trying the experiments to appearances which occurred in former ones, to which we are indebted for great part of the most curious facts in this paper. His endeavours have also been attended with much success, as he has not only shewn many remarkable circumstances relating to the freezing of the nitrous

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and vitriolic acids, and the phænomena of freezing mixtures; but has also produced degrees of cold greatly superior to any before known.

1. In the above-mentioned Paper I said, that the cold produced by mixing spirit of nitre with snow, is owing to the melting of the snow; and that in all probability there is a certain degree of cold, in which spirit of nitre is so far from dissolving snow, that it 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. A circumstance, however, which at first sight seems repugnant to this opinion, occurred in an experiment of FAHRENHEIT's for producing cold by a mixture of spirit of nitre and ice; namely, that the acid, which had been repeatedly cooled by different frigorific mixtures, was found frozen before it was mixed with the ice; notwithstanding which, cold was produced by the mixture. Professor BRAUN also found, that cold was produced by mixing frozen spirit of nitre with snow. On consideration, however, this appeared by no means inconsistent with the opinion there laid down, as there was great reason to think, that the freezing of the acid was of a different kind from that considered in the above-mentioned Paper, and that it did not proceed from the watery part separating from the rest and freezing; but that the whole acid, or perhaps the more concentrated part, froze; in which case it would not be extraordinary that the acid should dissolve more snow, and produce cold.

2. To clear up this point, I sent to Hudson's Bay a bottle of spirit of nitre, of nearly the same strength as FAHRENHEIT's; and desired Mr. M<sup>c</sup> NAB to expose it to the cold, and, if it froze, to ascertain the temperature, and decant the fluid part into  
another

another bottle, and send both home to be examined, as it would thereby be known, whether it was the whole acid, or only the watery part, which froze, For the same purpose also I sent some dephlogisticated spirit of nitre of the same strength, and also some strong oil of vitriol. I also sent some spirit of nitre and spirit of wine, both diluted with so much water, that it was expected, that with the cold of Hudson's Bay they would suffer the first kind of congelation; that is, their watery part would freeze, and thereby make the difference between the two kinds of freezing more apparent.

3. In the same Paper I say, "That on adding snow gradually to some of the spirit of nitre used by Mr. HUTCHINS, I found, 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 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 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 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.”

As it seemed likely that, by following this method, a greater degree of cold might be produced than had been done hitherto, I sent three other bottles of spirit of nitre and oil of vitriol, all three diluted, but not so much so, but that I thought they would require a little further dilution, in order to reduce them to their properest degree of strength. I also sent a bottle of highly rectified spirit of wine, and a mixture of equal quantities of the above-mentioned common spirit of nitre and oil of vitriol; and desired Mr. M<sup>c</sup> NAB. to find what degree of cold could be produced by mixing them with snow, after having first reduced them, in the above-mentioned manner, to their best degree of strength\*.

He was also desired to ascertain how much snow he added; for as their strength was determined before they were sent out, it would thereby be known what was the best strength of these liquors for frigorific mixtures.

\* This might have been done at home; but I thought it not unlikely that the strength found this way might differ, in some measure, according to the heat in which the experiment was tried.

All these bottles were numbered with a diamond; and as I shall sometimes distinguish them by these numbers, and as it may be of use to those who may consult the original, I have added the following list of these bottles, with their contents.

N <sup>o</sup>	Liquors mentioned in Art. 3.	Weight of marble which they dissolve.	Specific gravity at 60° of heat.
168	Spirit of nitre, . . . . .	,582	1,4371
27	Dephlogisticated spirit of nitre, . . . . .	,53	1,4040
103	Diluted oil of vitriol, . . . . .	,654	1,5596
28	Equal weights of N <sup>o</sup> 168. and N <sup>o</sup> 103. . . . .	- - -	- -
8	Very highly rectified spirit of wine, . . . . .	- - -	,8195
Liquors mentioned in Art. 2.			
151	Strong oil of vitriol, . . . . .	,98	1,8437
142	Spirit of nitre, . . . . .	,525	1,4043
139	Some of the same diluted with twice its weight of water, . . . . .	- - -	- -
141	Dephlogisticated spirit of nitre, . . . . .	,53	1,4033
143	Some of the same spirit of wine as in N <sup>o</sup> 8. diluted with 1½ its weight of water, . . . . .	- - -	- -
72	Diluted oil of vitriol for comparing the thermometers,	,629	- -
171	Oil of vitriol of about the usual strength, but the exact strength not known, intended to refresh the former when too weak.		

4. Professor BRAUN says, that by mixtures of snow and spirit of nitre he sunk thermometers filled with oil of saffras, and some other essential oils, to - 100° or - 124°; and that, by the same means, he sunk thermometers filled with the highest rectified spirit of wine to - 148°. Though there seemed great reason to think, from Mr. HUTCHINS's experiments, that there must be some mistake in this; yet, as it was possible that the essential oils, and even spirit of wine of a strength much different from that with which Mr. HUTCHINS's thermometers were filled, might follow a considerably different progression in their contraction:

contraction by great degrees of cold, I sent a thermometer filled with oil of saffaras, and two others with spirits of wine. One of these last was filled with the highest rectified spirits I could procure, its specific gravity at  $60^{\circ}$  of heat being ,8185; the other was intended to be filled with common spirits, though from circumstances I am inclined to suspect *that* also to have been filled with the best spirits. Besides these, there was sent a mercurial thermometer, accurately adjusted, according to the directions of the Committee of the Royal Society, printed in the LXVIIth volume of the Transactions; and also the two spirit thermometers used by Mr. HUTCHINS, which were filled with spirits whose specific gravity was ,8247.

5. These thermometers were compared together by exposing them to the cold, with their balls immersed in a glass vessel filled with diluted oil of vitriol. They were at times also compared in cold more violent than the natural cold of the climate, by adding snow to the acid in which they were tried, in which case care was taken to keep the mixture frequently stirred. Oil of vitriol was recommended for this purpose, as a fluid which would most likely bear any degree of cold without freezing, and whose natural cold might be much increased by the addition of snow. It seems to have answered the purpose very well, and not to have been attended with any inconvenience.

During the first comparison of these thermometers, a whitish globule, such as those which appear in frozen oil, was observed in the tube of the thermometer filled with oil of saffaras. This appearance of congelation did not much increase; but two days after a large air bubble was found in its ball, which prevented Mr. M<sup>c</sup> NAB from making further observations with it.

It is well known, that spirit of wine expands more by a given number of degrees of a mercurial thermometer in warm temperatures than in cold ones; and this inequality, as might be expected, was less in the stronger spirit than in the weaker, but the difference was inconsiderable. The oil of saffraas also had some of this inequality, but much less. It however appears to be by no means a proper fluid for filling thermometers with. No appearance was observed which indicates any considerable irregularity in the contraction of spirits of wine in intense cold, or which renders it probable, that thermometers filled therewith could be sunk by a mixture of snow and spirit of nitre to a degree near approaching to that mentioned by Professor BRAUN.

6. Mr. M<sup>c</sup> NAB in his experiments sometimes used one thermometer and sometimes another; but in the following pages I have reduced all the observations to the same standard; namely, in degrees of cold less than that of freezing mercury I have set down that degree which would have been shewn by the mercurial thermometer in the same circumstances; but as that could not have been done in greater degrees of cold, as the mercurial thermometer then becomes of no use, I found how much lower the mercurial thermometer stood at its freezing point, than each of the spirit thermometers, and increased the cold shewn by the latter by that difference.

*On the common and dephlogisticated Acids of Nitre.*

The following experiments shew, that both these acids are capable of a kind of congelation, in which the whole, and not merely the watery part, freezes. Their freezing point also differs

differs greatly according to the strength, and varies according to a very unexpected law. Like water too they bear being cooled very much below their freezing point before the congelation begins, and as soon as that takes place, immediately rise up to the freezing point.

7. On the morning of Feb. 1. the common and dephlogificated spirits of nitre, N<sup>o</sup> 142 and 141, whose specific gravities were 1,4043 and 1,4033, were found clear and fluid, the cold of the air at that time being  $-47^{\circ}$ . They also bore being shook without any alteration; but on taking out their stoppers, both of them in a few minutes began to freeze, the congelation beginning by a white appearance at top, which gradually spread to the bottom; and they became so thick as not to move on inclining the phial. For want of a thermometer whose ball reached far enough below its scale, Mr. M<sup>c</sup> NAB was not able to determine their cold while in the bottle; but in somewhat more than an hour's time, the frozen acid had so much subsided as to admit of his pouring a little fluid matter out of each into a glass with a thermometer in it\*; whereby the cold of the common spirit of nitre was found to be  $-31^{\circ}\frac{1}{2}$ , and that of the dephlogificated acid  $-30^{\circ}$ , the temperature of the air being  $-41^{\circ}$ . Each of these decanted liquors, at the time their temperature was tried, was full of small *spicula* of ice: they were then put into phials well stopped, and they, as well as the undecanted liquors, sent home to be examined. The decanted part of the common

\* It may be asked, why it was more possible to decant any liquor at this time than at first, as the acid was all the while exposed to a cold much below the freezing point? The reason in all probability is, not that any part of the ice first formed dissolved, but that the small filaments into which it shot collected together, and in some measure subsided to the bottom.



spirit of nitre dissolved ,535 of its weight of marble, and the undecanted part ,523; for which reason I shall call the strength of the former ,535, and that of the latter ,523; which mode of reckoning is observed in the remainder of this Paper. The strength of the decanted part of the dephlogificated acid was ,56, and that of the undecanted part ,528; so that it appears that in each of these acids the unfrozen part was a little stronger than the frozen part. It is remarkable, that in the common spirit of nitre, the decanted part, though stronger than the other, was paler coloured and less fuming.

8. On Dec. 21, the temperature of the air being  $-28^{\circ}$ , some dephlogificated spirit of nitre (N<sup>o</sup> 27.) of nearly the same strength as the former acid, was poured into a jar, in order to be diluted with snow, as recommended in Art. 2. Immediately after it was decanted, it began to freeze, in the same manner as before described, except that a less portion of it seems to have congealed: its temperature, tried by dipping a thermometer into it, was  $-19^{\circ}$ , where it remained stationary for many minutes; it was then diluted with snow, as will be mentioned in Art. 14. whereby its strength was reduced to 434.

9. On Dec. 29th, this diluted acid was completely melted, and half of it poured into a jar with a ground stopper, and both portions exposed to the air. In the morning they were perfectly fluid; but on taking the stopper out of the jar, and dipping in it a thermometer, the acid immediately froze, beginning by forming a white coat round the ball of the thermometer, which gradually spread through the whole fluid; and at the same time the thermometer rose till it stood stationary at  $-5^{\circ}$ . The cold of the acid before it began to freeze must have been about  $-30^{\circ}\frac{1}{2}$ , that being the temperature of a

glafs of vitriolic acid ftanding near it; but the thermometer which was dipped into it was five or fix degrees colder, which feems to be the caufe of the congelation beginning round the ball.

In the afternoon a thermometer was dipped into the other half of the acid, where, as the weather had grown lefs cold, it ftood above a minute at  $-25^{\circ}$ , without freezing; then, however, the acid froze, with the fame appearance as in the morning, and at the fame time the thermometer rofe to  $-4^{\circ}$ , and became ftationary.

This acid, being left in the air with the thermometer in it, was found in the evening at  $-45^{\circ}$ ; it however was not intirely frozen, being only thick as an unguent, which fhews that the unfrozen part muft have been of a different ftrength from the frozen part; but it does not appear whether ftonger or weaker. The next morning it was frozen folid, though the cold was only half a degree greater.

On Jan. 16th, this acid was again tried in the fame manner; it then fuffered a thermometer, whofe ball had been previoufly warmed in the hand, to be dipped into it, and remain there feveral minutes without freezing, though its temperature was  $-35^{\circ}$ . But on lifting up the thermometer, a drop fell from its ball into the acid, which immediately fet it a freezing, and it rofe up to  $-4^{\circ}\frac{1}{2}$ .

10. On Dec. 22d, the fpirit of nitre (N<sup>o</sup> 168.) which a few days before had been diluted with fnow, fo as to be reduced to the ftrength of ,411, was divided into two equal parts, and expofed to the cold. On Dec. 29th, when the temperature of the air was  $-17^{\circ}\frac{1}{2}$ , one of thefe parts was found beginning to freeze; the other was fluid, but began to freeze on dipping in a thermometer; the thermometer in both kept ftationary at

-  $1^{\circ}\frac{1}{2}$ . The latter was twice re melted and exposed to the cold, and both times the temperature of the frozen acid came out the same as before.

11. The white colour of the ice in these experiments seems owing only to its consisting of very slender filaments; for in some cases, where it froze slower, and where, in consequence, it shot into larger solid masses, they were transparent, and of the same colour as the acid itself. By the continuance of a sufficient cold, the acid, which by hasty freezing put on the white appearance, would become hard solid ice, but yet still retained its white appearance, owing perhaps to the filaments first shot consisting of an acid differing in strength from that which froze afterwards, and filled up the interstices.

In all these experiments, whether the ice was formed into minute filaments or solid masses, still, whenever there was a sufficient quantity of fluid matter to admit of it, they constantly subsided to the bottom; a proof that the frozen part was heavier than the unfrozen. The difference indeed is so great, that in one case where it froze into solid crystals on the surface, these crystals, when detached by agitation, fell with force enough to make a tinkling noise against the bottom of the glass.

These acids contract very much on freezing. Whenever the acid is frozen solid, the surface, instead of being elevated in ridges, like frozen water, is depressed and full of cracks. In one experiment Mr. M<sup>c</sup> NAB, after a glass almost full of acid was nearly frozen, filled it to the brim with fresh acid; and then, after it was completely frozen, the surface was visibly depressed, with fissures one-eighth of an inch broad, extending from top to bottom. It is this contraction of the acid in freezing which makes the frozen part subside in the fluid

part; as it was found, in the undiluted acid, that the latter consisted of a stronger, and consequently heavier, acid than the former. But still the subsidence of the frozen part shews, that the ice is not mere water, or even a very dilute acid; which indeed was proved by the examination of the liquors sent home.

The ninth and tenth articles shew, that though the acids bear being cooled greatly below the freezing point, without any congelation taking place, yet as soon as they begin to freeze they immediately rise up to their freezing point; and this point is always very nearly, if not exactly, the same in the same acid; for those acids were frozen and melted again three or four times, and were cooled considerably more below the freezing point in one trial than another, and yet as soon as they began to freeze the thermometer immersed in them constantly rose nearly to the same point.

The quantity which these acids will bear being cooled below the freezing point, without freezing, is remarkable. The diluted spirit of nitre, whose freezing point is  $-1^{\circ}\frac{1}{2}$ , once bore being cooled to near  $-39^{\circ}$ , without freezing, that is, near 37 degrees below its freezing point. The diluted dephlogificated spirit of nitre, whose freezing point is  $-5^{\circ}$ , bore cooling to  $-35^{\circ}$ ; and the dephlogificated spirit of nitre (141) whose true freezing point is most likely  $-19^{\circ}$  (*see next article*) bore being cooled to  $-49^{\circ}$ : perhaps too they might have born to be cooled considerably lower without freezing, but how much does not appear. It must be observed, however, that the same diluted spirit which at one time bore being cooled to  $-39^{\circ}$ , at another froze, without any apparent cause, when its cold was certainly less than  $-30^{\circ}$ , and most likely not much below  $-18^{\circ}$ .

12. The freezing point differs remarkably, according to the strength of the acid. In the diluted dephlogificated and common spirit of Art. 7. and 8. the freezing point was  $-5^{\circ}$  and  $-1^{\circ}\frac{1}{2}$ . In the dephlogificated and common spirit of Art. 5. the decanted parts of which were stronger than the foregoing in scarcely so great a proportion as that of four to three, it seemed to be  $-30^{\circ}$  and  $-31^{\circ}\frac{1}{2}$ . It may indeed be suspected, that as this point was determined only by pouring a small quantity of the acid into a glass, at a time when the air and glass were much colder than the acid, these decanted liquors might be cooled by the air and glass, and thereby make the freezing point appear lower than it really was: but I do not think this could be the case; for as the decanted liquors were full of small filaments of ice, they could hardly be cooled sensibly below their freezing points without freezing; and any cold, communicated to them by the air or glass, would serve only to convert more of them into ice, without sensibly increasing their cold: so that I think this experiment determines the true freezing point of their decanted part; but it must be observed, that as the decanted part was rather stronger than the rest, it is very possible that the freezing point of the undecanted part might be considerably less cold.

A circumstance which might incline one to think, that the way by which the freezing point was determined in this experiment is defective is, that the freezing point of the dephlogificated acid N<sup>o</sup> 27. though nearly of the same strength as that last mentioned, but rather stronger, was much less low, being only  $-19^{\circ}$ . But I have little doubt that the true reason of this is, that in the former acid the strength of the decanted part, which is the part whose freezing point was tried, was found to be at least  $\frac{1}{20}$  greater than that of the whole mass; whereas  
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in N<sup>o</sup> 27. the fluid part was in all probability not sensibly stronger than the whole mass; for as N<sup>o</sup> 27. was cooled only seven degrees below the freezing point, and its temperature was tried soon after its beginning to freeze, not much of the acid could have frozen; whereas the other was cooled 15 degrees below its freezing point, and was exposed for an hour or two to an air not much less cold, in consequence of which a considerable part of the acid must have frozen; so that in all probability the acid, whose freezing point was found to be  $-30^{\circ}$ , was in reality  $\frac{1}{20}$  part stronger than that whose freezing point was  $-19^{\circ}$ .

If this reasoning be just, the freezing point of these acids is as follows:

		Freezing point.	
Dephlogificated spirit of nitre, whose strength =	{	,56	$-30^{\circ}$
		,53	$-19$
		,437	$-4\frac{1}{2}$
Common spirit of nitre, whose strength =	{	,54	$-3\frac{1}{2}$
		,411	$-1\frac{1}{2}$

*On the Phenomena observed on mixing Snow with these Acids.*

13. On Dec. 13, snow was added to the spirit of nitre N<sup>o</sup> 168, as recommended in Art. 2. The snow was put in very gradually, and time was taken to find what effect each addition had on the thermometer and mixture, before more was added. The temperature of the acid before the mixture was  $-27^{\circ}$ , and each addition of snow raised the thermometer a little, till it rose to  $-1^{\circ}\frac{1}{4}$ ; after which the next addition made it sink to  $-2^{\circ}$ , which shewed that sufficient snow had then been added. The quantity

quantity of snow used was pretty exactly  $\frac{4}{10}$  of the weight of the acid, the weight of the acid being 13 oz. so that the strength of the diluted acid was reduced to ,411.

The acid before the addition of snow had no signs of freezing, its temperature being in all probability much above its freezing point; yet the snow did not appear to dissolve, but formed thin white cakes, which however did not float on the surface, but fell to the bottom, and when broke by the spatula formed a gritty sediment; so that it appears, that these cakes are not simply undissolved snow, but that the adjoining acid absorbed so much of the snow in contact with it, as to become diluted sufficiently to freeze with that degree of cold, and then congealed into these cakes. The quantity of congealed matter seems to have kept increasing till the end of the experiment.

14. On Dec. 21, an experiment was made in the same manner with the dephlogisticated spirit of nitre N<sup>o</sup> 27. The acid began to freeze in pouring it into the jar in which the mixture was to be made, and stood stationary there at  $-19^{\circ}$ , as related in Art. 6.; so that the liquor at the beginning of the experiment was white and thick, which made the effect of the addition of the snow less sensible. However, the congealed matter constantly subsided to the bottom, and the quantity seems to have continued increasing to the end of the experiment. The heat of the mixture rose to  $-4^{\circ}$  before cold began to be produced, and the quantity of snow added was  $\frac{2.2}{10.2}$  of that of the acid, so that the strength of the acid was reduced to ,437 by the dilution.

A very remarkable circumstance in this experiment is, that the acid, while the snow was adding, first became of a yellowish,

lowish, and afterwards of a greenish or bluish hue. This colour did not go off by standing, but continued at least ten days, during which time the acid constantly kept that colour, except when by hasty freezing it shot into small filaments, in which case it put on the white appearance which these acids always assumed under those circumstances; but once that by gradual freezing it shot into transparent ice, this ice was of a bluish colour.

It is difficult to conceive what this colour should proceed from. Spirit of nitre is well known to assume this colour when much phlogisticated and properly diluted; but one does not see why it should become phlogisticated by the addition of the snow, and still less why the dephlogisticated acid should become more phlogisticated thereby than the common acid did; for though it is not extraordinary, that a process not capable of producing any increase of phlogistication in the common acid, should make this as much phlogisticated as that, yet it is very extraordinary that it should make it more so. No notice is taken of any effervescence or discharge of air while it was assuming this colour, nor was it observed that it became more smoking thereby, or that the top of the phial in which it was kept became full of red fumes, as might naturally be expected if it was rendered much phlogisticated. These are circumstances which, considering Mr. M<sup>c</sup> NAB's great attention to set down all the phænomena that occurred, I should think would hardly have been omitted if they had really happened.

15. It is remarkable, that in both these experiments the addition of snow produced heat, until it arrived pretty exactly at what was found to be the freezing point of the diluted acid; but that as soon as it arrived at that point, the addition of more snow began to produce cold. This can hardly be owing merely



merely to accident, and to both acids having happened to be of that precise degree of heat before the experiment began, that their heat after dilution should coincide with the freezing point answering to their new strength. The true cause seems to be as follows. It will be shewn in Art. 16. and 17. that the freezing point of these acids, when diluted as in the foregoing experiments, is much less cold than when they are considerably more diluted; and it was before shewn to be much less cold than when not diluted; so that there must be a certain degree of strength, not very different from that to which these acids were reduced by dilution, at which they freeze with a less degree of cold than when they are either stronger or weaker. Now in these experiments, the temperature of the liquors before dilution was below this point of easiest freezing, and a great deal of the acid was in a state of congelation all the time of dilution; the consequence of which is, that when they were diluted to the strength of easiest freezing, they would also be at the heat of easiest freezing; for they could not be below that point, because, if they were, so much of the acid would immediately freeze as would raise them up to it; and they could not be above it, for, if they were, so much of the congealed acid would dissolve as would sink them down to it. After they were arrived at this strength of easiest freezing, the addition of more snow would produce cold, unless this strength be greater than that at which the addition of a small quantity of snow begins to produce cold; but even were this the case, heat would not be produced, but the temperature of the acids would remain stationary until they were so much diluted that the addition of more snow should produce cold. So that, in either case, the heat of the acids, at the time that the addition of fresh snow began to produce cold, must be that of easiest freezing;

freezing; and consequently, as this heat was found to coincide very nearly with the freezing point of these acids, after dilution, it follows that their strengths at that time could differ very little from the strength of easiest freezing.

If the temperature of the liquors at the beginning of the experiment had been above the point of easiest freezing, none of the acid would have congealed during the dilution, and nothing could have been learnt from the experiment relating to the point of easiest freezing; but the heat would have kept increasing, till the acid was diluted to that degree of strength at which the cold produced by the dissolving of the snow was just equal to the heat produced by the union of the melted snow with the acid\*; after which the addition of more snow would begin to produce cold. When I recommended this method of finding the best strength of spirit of nitre for producing cold, by the addition of snow, I was not aware of any impediment from the freezing of the acid, in which case it would have been a very proper method; but on account of this circumstance it can hardly be considered as such, except when the cold of the acid at setting out is less than that of easiest freezing.

In the dephlogisticated spirit of nitre the freezing points answering to the strength of ,434, ,53, and ,56, were said to be  $-4^{\circ}\frac{1}{2}$ ,  $-19^{\circ}$ , and  $-30^{\circ}$ ; and the differences of  $-30^{\circ}$  and  $-19^{\circ}$  from  $-4^{\circ}\frac{1}{2}$  are to each other very nearly in the duplicate ratio of ,126 and ,096, the differences of the corresponding strengths from ,434; which, as ,434 is the strength of easiest freezing, is the proportion that might naturally be

\* In the experiment related in my observations on Mr. HUTCHINS'S Experiments, this strength was rather greater than that of easiest freezing: but whether it is so in degrees of cold exceeding that in which my experiment was tried, does not appear.

expected, and consequently serves in some measure to confirm the reasoning in this and the 12th Article.

16. After Mr. M<sup>c</sup> NAB had diluted these acids as above-mentioned, he divided each of them into two parts, and tried what degree of cold could be produced by mixing them with snow. On January 15th, one of these parts of the common spirit of nitre was tried. It was fluid when the experiment began, though its temperature, as well as that of the snow, was  $-21^{\circ}\frac{1}{2}$ ; but on adding snow it immediately began to freeze, and grew thick, and its heat increased to  $-2^{\circ}\frac{1}{2}$ ; but by the addition of more snow it quickly funk again, and at last got to  $-43^{\circ}\frac{1}{4}$ . During the addition of the snow, the mixture grew thinner, and by the time it arrived at nearly the greatest degree of cold, consisted visibly of three parts: the lowest part, which consisted of frozen acid, was white and felt gritty; the upper part, which occupied about an equal space, was also white, but felt soft, and must have consisted of unmelted snow; the other part, which occupied by much the smallest space, was clear and fluid. The quantity of snow added was about  $\frac{1}{3}$  of the weight of the acid, and consequently its strength was reduced to ,243.

Though snow was added to the acid in this experiment as long as, and even longer than, it produced any increase of cold, yet some days after, on adding more snow to the mixture, while it was fluid, and of the temperature of  $-45^{\circ}\frac{3}{4}$ , the cold was increased to  $-44^{\circ}\frac{1}{4}$ , or 1 degree lower than before. Mr. M<sup>c</sup> NAB did not perceive the snow to melt, though in all probability some must have done so, or no cold would have been produced.

The cause of this seems to be, that in the preceding experiment the congealed part of the acid was stronger than the

fluid part; so that, though the fluid part was not strong enough to dissolve snow in a cold greater than  $-43^{\circ}\frac{1}{4}$ , yet the whole acid together was strong enough to do it in a cold one degree greater.

A circumstance occurred in the last experiment which I cannot at all see the reason of; namely, a small part of the acid being poured into a saucer, before the addition of the snow, it was in an hour's time changed into solid ice, though the cold of the air, at the time the acid was poured out, was only  $-41^{\circ}\frac{1}{4}$ , and does not seem to have increased during the experiment.

17. On December 30, the other half of the same acid had been tried in the same manner; at the beginning of the experiment not more than one-ninth part of the acid was fluid, the rest solid clear ice; its temperature was  $-34^{\circ}\frac{1}{2}$ , and that of the snow nearly the same; the greatest degree of cold produced was  $-42^{\circ}\frac{3}{4}$ ; and the quantity of snow employed was about one-eighteenth of the weight of the acid; so that the strength of the mixture was ,38. The freezing point of the acid thus diluted appears to be about  $-45^{\circ}\frac{1}{4}$ ; for by the increase of warmth during the day-time, most of the congealed matter dissolved; but in the evening it began to freeze again, so as to become thicker, its temperature being then  $-45^{\circ}\frac{1}{4}$ ; and the next morning it was frozen solid, its cold being one degree greater.

18. On December 12, the diluted spirit of nitre N<sup>o</sup> 139, whose strength was ,175, was found frozen, its temperature being  $-17$ . The fluid part, which was full of thin flakes of clear ice, and was of the consistence of syrup, was decanted into another bottle, and sent back. Its strength was ,21, and was greater than that of the undecanted part in the proportion of ,21 to ,16; so that, as not much of the undecanted part was

really congealed, the frozen part of the acid must have been much weaker than the rest, if not mere water. Accordingly, during the melting of the undecanted part, the frozen particles swam at top. Mr. M<sup>c</sup> NAB added snow to a little of the decanted liquor, but it did not dissolve, and no increase of cold was produced.

19. From these experiments it appears, that spirit of nitre is subject to two kinds of congelation, which we may call the aqueous and spirituous; as in the first it is chiefly, if not entirely, the watery part which freezes, and in the latter the spirit itself. Accordingly, when the spirit is cooled to the point of aqueous congelation, it has no tendency to dissolve snow and produce cold thereby, but on the contrary is disposed to part with its own water; whereas its tendency to dissolve snow and produce cold, is by no means destroyed by being cooled to the point of spirituous congelation, or even by being actually congealed. When the acid is excessively dilute, the point of aqueous congelation must necessarily be very little below that of freezing water; when the strength is ,21, it is at  $-17^{\circ}$ , and at the strength of ,243, it seems, from Art. 16. to be at  $-44^{\circ}\frac{1}{4}$ . Spirit of nitre, of the foregoing degrees of strength, is liable only to the aqueous congelation, and it is only in greater strengths that the spirituous congelation can take place. This seems to be performed with the least degree of cold, when the strength is ,411, in which case the freezing point is at  $-1^{\circ}\frac{1}{2}$ . When the acid is either stronger or weaker, it requires a greater degree of cold; and in both cases the frozen part seems to approach nearer to the strength of ,411 than the unfrozen part; it certainly does so, when the strength is greater than ,411, and there is little doubt but what it does so in the other case. At the strength of ,54 the point of spirituous congelation.

congelation is  $31^{\circ}\frac{1}{2}$ , and at ,33 probably  $-45^{\circ}\frac{3}{4}$ ; at least one kind of congelation takes place at that point, and there is little doubt but that it is of the spirituous kind. In order to present this matter more at one view, I have added the following table of the freezing point of common spirit of nitre answering to different strengths.

Strength.	Freezing point.	
,54	$-31^{\circ}\frac{1}{2}$	} spirituous congelation.
,411	$-1^{\circ}\frac{1}{2}$ *	
,38	$-45^{\circ}\frac{3}{4}$	
,243	$-44^{\circ}\frac{3}{4}$	} aqueous congelation.
,21	$-17$	

20. In trying the first half of the dephlogificated spirit of nitre, the cold produced was  $-44^{\circ}\frac{1}{2}$ . The acid was fluid before the addition of the snow, and of the temperature of  $-30^{\circ}$ , but froze on putting in the thermometer, and rose to  $-5^{\circ}$ , as related in Art. 7.

In trying the second part, the acid was about  $0^{\circ}$  before the addition of the snow, and therefore had no disposition to freeze. The cold produced was  $-42^{\circ}\frac{1}{2}$ .

As the quantity of snow added in these experiments was not observed, they do not determine any points of aqueous or spirituous congelation in this acid; but there is reason to think, that these points are nearly the same as those of common spirit of nitre of the same strength, as the cold produced in these experiments was nearly the same as that obtained by the common spirit of nitre.

\* The point of easiest freezing.

*On the Vitriolic Acid.*

21. On December 12, the strong oil of vitriol N° 151. was found frozen, and was nearly of the colour and consistence of hogs-lard. Its temperature, found by pressing the ball of a thermometer into it, was  $-15^{\circ}$ , and that of the air nearly the same; but in the night it had been exposed to a cold of  $-33^{\circ}$ . It dissolved but slowly on being brought into a warm room, and was not completely melted before it had risen to  $+20^{\circ}$ , and even then was not very fluid, but of a syrupy consistence. During the progress of the melting, the congealed part sunk to the bottom, as in spirit of nitre; and many air bubbles separated from the acid, which, when it was completely melted, formed a little froth on the surface. As soon as it was sufficiently melted to admit of it, which was not till it had risen to the temperature of  $+10^{\circ}$ , the fluid part was decanted, and both were sent home to be examined.

It is remarkable, that the frozen part did not intirely dissolve until the temperature was so much increased. This would incline one to think, that the frozen part must have differed in some respect from the rest, so as to require much less cold to make it freeze; but yet I could not find that the strength of the decanted part differed sensibly from the rest.

It appeared by another bottle of oil of vitriol, which also froze by the natural cold of the air, that this acid, as well as the nitrous, contracts in freezing.

22. On December 21, when the weather was at  $-30^{\circ}$ , the vitriolic acid N° 103. was diluted with snow, as directed in Art. 3. The snow dissolved immediately, and no signs of congelation appeared during any part of the process. The  
temperature

temperature of the acid rose only one degree before it began to sink, and the weight of the snow added was only  $\frac{1}{12}$  of that of the acid, so that its strength was reduced thereby to ,605; which is therefore the best degree of strength for producing cold by the addition of snow, when the degree of cold set out with is  $-30^{\circ}$ . This strength is one-fifteenth part less than what I found myself, by a similar experiment, when the temperature of the acid was  $+27^{\circ}$ ; which shews, that the best degree of strength is rather less, when the degree of cold set out with is great than when small, but that it does not differ much.

23. The acid thus diluted was divided into two parts, and the next day Mr. M<sup>c</sup> NAB tried what degree of cold could be produced by adding snow to one of them. The temperature of the air at the time was  $-39^{\circ}$ , and the mixture sunk by the process to  $-55\frac{1}{2}$ . The snow dissolved readily, and the mixture did not lose much of its fluidity until it had acquired nearly its greatest degree of cold, nor did any congealed matter sink to the bottom in any part of the process. The quantity of snow added was about  $\frac{8}{100}$  of the weight of the acid, so that the strength of the mixture was about ,325.

24. On January 11, thin crystals of ice were found diffused all through this mixture, the temperature of the air being  $-51\frac{1}{2}$ , but that of the liquor was not tried. As this congelation must have been of the aqueous kind, and seems to have taken place at the temperature of  $-51\frac{1}{2}$ , it should follow, that this acid had no power of dissolving snow in a cold of  $51\frac{1}{2}$ ; so that it does not at first appear why a cold four degrees greater than that should have been produced in the foregoing experiment. The reason is, that at the time the mixture arrived at  $-55\frac{1}{2}$ , it appeared by the diminution of its fluidity to have contained



contained some undissolved snow, and some more was added to it after that time, which before the first of January dissolved and mixed with the acid; so that the acid in the mixture, at the time it sunk to  $-55^{\circ}\frac{1}{2}$ , was not quite so much diluted as that which froze on January 1. This is the reverse of what happened in the trial of the nitrous acid in Art. 15. as in that experiment the fluid part, at the time of the greatest cold, was weaker than the whole mixture together; but it must be considered, that *that* mixture contained much congealed acid, as well as undissolved snow, whereas *this* contained only the latter.

25. On January 1, snow was added to the other half of the acid diluted on December 21. The cold produced was much greater than before, namely  $-68^{\circ}\frac{1}{2}$ ; this seems to have proceeded, partly from the air and materials having been 12 degrees colder in this than in the former experiment, and partly from the snow having been added faster, so that the mixture arrived at its greatest degree of cold in 20', whereas it before took up 46'. Another reason is, that the former mixture was made in too small a jar, in consequence of which it was poured into a larger before the experiment was completed, whereby some cold was lost. The quantity of snow used in this experiment was less than in the former, so that the strength of the acid after the experiment was about ,343. The mixture also grew much thicker, and had a degree of elasticity resembling jelly; but whether this was owing only to more snow remaining undissolved, or to any other cause, I cannot tell.

26. Great as the foregoing degree of cold is, Mr. M<sup>c</sup> NAB, on February 2, produced one much greater. In hopes of obtaining a greater degree of cold by previously cooling the materials, he cooled about seven ounces of oil of vitriol, whose strength was ,629, that is, rather stronger than the foregoing,

by placing the jar in which it was contained in a freezing mixture of oil of vitriol and snow; the snow intended to be used was also cooled by placing it under the vessel in which the freezing mixture was made. As soon as the acid in the jar was cooled to the temperature of  $-57^{\circ}\frac{1}{2}$ , a little of the snow was added, on which it immediately began to freeze, and rose to  $-36^{\circ}$ ; but in about 40 minutes, as the jar was still kept in the freezing mixture, it sunk to  $-48^{\circ}$ ; by which time it was grown very thick and gritty, especially at bottom. More of the cooled snow was then added, which in a short time made it sink to  $-78^{\circ}\frac{1}{2}$ , and at the same time the thickness and tenacity of the mixture diminished; so that by the time it arrived at the greatest degree of cold, very little thickness remained.

It is worth inquiring, what was the reason of the greater degree of cold produced in this than in the preceding experiment? It could not be owing to the materials being colder; for at the time of the second addition of snow, at which time the experiment may be considered to have begun, the acid was not colder than at the beginning of the preceding experiment, and the snow in all probability not much colder. It could not be owing neither to the jar having been kept in the freezing mixture: for though that mixture was three or four degrees colder than the air in the preceding experiment, yet the acid in the jar, before it acquired much addition of cold, would be robbed of its cold faster by the mixture than it would by air of the same temperature as that in the preceding experiment. Neither could it proceed from any difference in the strength of the acid; for what difference there was must have done more hurt than good. The true reason is, that the acid was in a state of congelation: for as the congealed acid united to the snow and became fluid by the union, it is plain, that cold must have been produced both  
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by the melting of the snow and by that of the acid; whereas, if the acid had been in a fluid state, cold would have been produced only by the first cause, and consequently a greater degree of cold should be produced in this experiment than in the former. The only inconvenience attending the acid being in a state of congelation is, that in all probability it does not unite to the snow so readily as when in a fluid state; but the difference seems not material, as the cold was produced, and the materials melted, in 5 minutes.

27. The day before, Mr. M<sup>c</sup> NAB, by adding snow to some of the same acid in the usual manner, when the cold of the materials was  $-46^{\circ}$ , produced a cold of only  $-66^{\circ}$ .

28. In these four last experiments the acid was reduced, by the addition of the snow, to the strengths of ,325, ,343, ,403, and ,334; and the cold produced in them was before said to be  $-55^{\circ}\frac{1}{2}$ ,  $-68^{\circ}\frac{1}{2}$ ,  $-78^{\circ}\frac{1}{2}$ , and  $-66^{\circ}$ ; whence we may conclude, that these are nearly the points of aqueous congelation answering to the foregoing strengths; only it appears, from what was said in Art. 24. that the strengths here set down are all of them rather too small.

Though it is certain that oil of vitriol is capable of the spirituous congelation, and though it appears, both from the foregoing experiments and from some made by the Duc D'AYEN\* and by M. DE MORVEAU †, that it freezes with a less degree of cold when strong than when much diluted, it is not certain whether it has any point of easiest freezing, like spirit of nitre, or whether the cold required to freeze it does not continually diminish as the strength increases, without limitation; but the latter opinion is the most probable. For the Duc D'AYEN's and

\* Diction. de Chym. par MACQUER, 2<sup>de</sup> edit.

† Nouv. Mém. de l'Académ. de Dijon, 1782, 1<sup>er</sup> semestre, p. 68.

M. DE MORVEAU'S acids, which, as they were concentrated on purpose, were most likely stronger than Mr. M<sup>c</sup> NAB'S, froze with a cold less than zero of FAHRENHEIT; whereas the freezing point of Mr. M<sup>c</sup> NAB'S undiluted acid, whose strength was ,98, was  $-15^{\circ}$ , and that of the diluted acid, whose strength was ,629, was  $-36^{\circ}$ ; and when the acid was more diluted, it was found to bear a much greater cold without freezing. It appears also, both from Art. 21. and from M. DE MORVEAU'S experiment, that during the congelation of the oil of vitriol, some separation of its parts takes place, so that the congealed part differs in some respect from the rest, in consequence of which it freezes with a less degree of cold; and as there is reason to think from Art. 21. that these two parts do not differ much in strength, it seems as if the difference between them depended on some less obvious quality, and probably on that, whatever it is, which forms the difference between glacial and common oil of vitriol. The oil of vitriol prepared from green vitriol, has sometimes been obtained in such a state as to remain constantly congealed, except when exposed to a heat considerably greater than that of the atmosphere, whence it acquired its name of *glacial* \*. It is not known indeed upon what this property depends, but it is certainly something else than its strength; for oil of vitriol of this kind is always smoking, and the fumes it emits are particularly oppressive and suffocating, though very different from those of the volatile sulphureous acid. On rectification likewise it yields, with the gentlest heat, a peculiar concrete substance, in the form of saline crystals; and after this volatile part has been driven off,

\* Mém. de l'Académ. des Sc. 1738, p. 288.

the remainder is no longer smoking, and has lost its glacial quality\*.

*On the Mixture of Oil of Vitriol and Spirit of Nitre.*

29. This mixture is not so fit for producing cold by the addition of snow, as oil of vitriol alone; for the cold obtained did not exceed  $-54^{\circ}\frac{1}{2}$ , in either of the experiments tried with it. The point of spirituous congelation of this mixture, when diluted with somewhat more than one-tenth of its weight of water, is about  $-20^{\circ}$ , and is much lower when the acid is considerably more diluted: but as the Society will most likely have less curiosity about the disposition to freeze of this mixture than of the simple acids, I shall spare the particulars.

*On the Spirit of Wine.*

30. The rectified spirits N<sup>o</sup> 8. were diluted with snow, in the same manner as the other liquors; but were found not to want any, as the first and only addition of snow produced cold. The quantity added was about  $\frac{1}{28}$  of the weight of the spirit.

31. The spirit thus diluted was divided, like the other liquors, into two parts, and each tried separately. The first was at  $-45^{\circ}$ , before the addition of the snow, and was sunk by the process to  $-56^{\circ}$ . The snow, even at the first addition, did not dissolve well, so that the spirit immediately

\* CRELL's Neu. Entdeck. in der Chemie, Th. 11. p. 100. Th. 12. p. 241, &c. and Annalen, 1785, St. 5. p. 438, &c.

became full of white spots \*, and grew thick by the time it arrived at its greatest degree of cold. After standing some hours, the mixture rose to the temperature of  $-39^{\circ}$ , and was grown clear, but yet was not limpid, but of the consistence of syrup. No cold was produced by adding snow to it in that state, though it appeared that its point of aqueous congelation was at least 6 degrees lower than its temperature at that time †; which seems to shew that spirit of wine has scarce any power of dissolving snow when it wants even 6 degrees of its point of aqueous congelation, and therefore is another instance that snow is dissolved much less readily by spirit of wine than by the nitrous and vitriolic acids.

32. In trying the other part of the diluted spirits, the cold produced was only  $-47^{\circ}\frac{1}{2}$ , the cold set out with being  $-37^{\circ}$ .

33. It appeared by the diluted spirit of wine N<sup>o</sup> 143. which on December 12 froze by the natural cold of the atmosphere, and was treated in the same manner as the diluted spirit of nitre, that when highly rectified spirit of wine, such as N<sup>o</sup> 8. is diluted with  $1\frac{4}{10}$  its weight of water, its point of aqueous congelation will be at  $-21^{\circ}$ . The congealed part of the spirit was white like diluted milk, and even the decanted part, which was full of thin films of ice, had a milky hue. The fluid part was stronger than the rest, and no increase of cold was produced by adding snow to some of it, both of which are marks of aqueous congelation.

\* This was not the case during the above-mentioned dilution of the spirits; but the cold was 16 degrees less in that experiment than in this.

† On account of the dilution which the spirits suffered by the melting of the snow which remained undissolved at the time of the greatest cold, its point of aqueous congelation was no longer so low as  $-56^{\circ}$ ; but it still was not less than  $-45\frac{1}{2}$ , as in the evening it was found at that temperature, without much congealed matter in it.

Though the foregoing experiments confirm the truth of what I said, in the account of Mr. HUTCHINS's experiments, concerning the cause of the cold produced by mixing snow with different liquors, and intirely clear up the difficulty relating to it which I mentioned in Art. 1. yet several questions may naturally occur; such as, why the cold produced by the oil of vitriol was so much greater than that obtained by the spirit of nitre, notwithstanding that in warmer climates the nitrous acid seems to produce more cold? and why the cold produced by the nitrous acid, notwithstanding its previous dilution, which might naturally be expected to be of service, was not greater than has been obtained by other persons without that precaution? But as this would lead me into disquisitions of considerable length, without my being able to say any thing very satisfactory on the subject, I shall forbear entering into it. I will only observe, that in most of the foregoing experiments, Mr. M<sup>c</sup> NAB would probably have produced more cold, if he had added the snow faster. We ought not, however, to regret that he did not, as its effects on the acids would then have been less sensible.

The natural cold, when these experiments were made, is remarkable; as there were at least nine mornings in which the cold was not less than that of freezing mercury; four in which it was at least eight degrees below that point, or  $-47^{\circ}$ ; and one in which it was  $-50^{\circ}$ . Whereas out of nine winters, during which Mr. HUTCHINS observed the thermometer at Albany Fort, there were only twelve days in which the cold was equal to that of freezing mercury, and the greatest cold seems to have been  $-45^{\circ}$ . I cannot learn whether the last winter was more severe than usual at Hudson's Bay; or whether Henley-House is a colder situation than Albany, which  
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may perhaps be the case; for though it is only 130 miles distant from it, yet it stands inland, and to the W. or S.W. of it, which is the quarter from which the coldest winds blow.

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Mr. M<sup>c</sup> NAB's original account of the experiments which furnished the materials of this Paper, having been thought too long to be printed in detail, is deposited in the Archives of the Society.

**END OF PART I. OF VOL. LXXVI.**