XXV. *Experiments on the Production of artificial Cold. By Mr.* Richard Walker, *Apothecary to the* Radcliffe Infirmary *at* Oxford. *In a Letter* to Henry Cavendish, *Esq. F.R.S. and A.S.*

Read June 5, 1788.

THE Royal Society having been pleased to insert, among their Transactions for last year, an account of some experiments of mine, relating to the production of artificial cold, transmitted in a letter from Dr. BEDDOES, I am induced to mention a few I have made since.

Your zealous attention to this subject, under whose auspices this, as well as other branches of natural philosophy, hath received considerable improvement, will, I hope, apologize for the liberty I have taken in addressing myself to you, especially since any new and useful facts I may have ascertained are principally owing to those endeavours your excellent Papers have incited in me.

My most powerful frigorific mixture is the following:

Of strong fuming nitrous acid, diluted with water (rain or distilled water is best) in the proportion of two parts of the former to one of the latter, each by weight, well mixed, and cooled to the temperature of the air, three parts; of vitriolated natron (GLAUBER's salt) four parts; of nitrated ammonia (nitrous ammoniac) three and a half parts, each by weight, reduced separately to fine powder: the powdered vitriolated natron is to be added to the diluted acid, the mixture well ſtirred, and immediately afterward the powdered nitrated ammonia, again ſtirring the mixture: to produce the greateſt effect, the ſalts ſhould be procured as dry and tranſparent as poſſible, and uſed freſhly powdered. Theſe ſeem to be the beſt proportions when the temperature of the air and ingredients is +50°; as the temperature at ſetting out is higher or lower than this, the quantity of the diluted acid will evidently require to be proportionably diminiſhed or increaſed. This mixture is but little inferior to one made by diſſolving ſnow in nitrous acid, for it ſunk the thermometer from +32° to −20°; perhaps it may be poſſible to reduce the ſalts to ſo fine a powder as to make it equal. In this laſt experiment the diluted acid was equal in quantity to the vitriolated natron, being four parts each, the nitrated ammonia three and a half as before. A powder compoſed of muriated ammonia (crude ſal ammoniac) five parts, nitrated kali (nitre) four parts, mixed, may be ſubſtituted in the ſtead of nitrated ammonia, with nearly equal effect, and in the ſame proportion.

Cryſtallized nitrated ammonia, reduced to very fine powder, ſunk the thermometer, during its ſolution in rain-water, forty-eight degrees, from +56°, the temperature of the air and materials, to +8°; and when evaporated gently to dryneſs, and finely powdered, it ſunk the thermometer forty-nine degrees, to +7°, the temperature of the air and materials being as before at +56°: therefore, in this ſalt (which produces, as appears above, much greater cold during ſolution in water, than any other hitherto known) the water of cryſtallization is not in the leaſt conducive to that effect. I expected, that by diluting the ſtrong nitrous acid to the proper ſtrength with ſnow, inſtead of water, by which its temperature would be much reduced,

reduced, and then adding the ſalts, a much greater degree of cold might be produced; but, by various diverſified trials, I found but little advantage gained; I ſhall therefore forbear mentioning the particulars. In the courſe of this winter, ſome diluted nitrous acid, in a wide-mouthed phial, was immerſed in a freezing mixture; when cooled to about $-32°$, it froze intirely to the conſiſtence of an ointment, when the thermometer ſuddenly roſe to $-2°$; on adding ſome ſnow that lay by me, it became again liquid, and the mercury ſunk into the bulb of a thermometer graduated to $-76°$: I know not its exact ſtrength; but by the effect imagine it might correſpond nearly with that which is capable of the eaſieſt point of ſpirituous congelation. Cold, I have found, may be produced by the union of ſuch ſalts as on mixing are decompoſed, and become liquid or partially ſo. The mineral alkali produces this effect with all the ammoniacal ſalts; but with nitrated ammonia to a conſiderable degree. The mineral alkali added in powder to nitrous acid, diluted as above, ſunk the thermometer twenty-two degrees only, from 53° (temperature of air and materials) to 31°. This ſalt contains nearly as much water of cryſtallization as vitriolated natron, and produces more cold during ſolution in water than that ſalt. The reaſon why it produces leſs when added to acid than the neutral ſalt does, is perhaps ſufficiently evident. I have obſerved the thermometer to be ſtationary, or even to riſe, during the violent efferveſcence produced on mixing thoſe materials, and to ſink as ſoon as that ceaſed.

Vitriolated natron diſſolved indifferently in rectified ſpirit of wine, and produced neither heat or cold; the diſpoſition to produce cold, during its ſolution, being perhaps exactly counteracted by the tendency which the diſſolved ſalt hath in

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uniting with the ſpirit to produce heat. Vitriolated magneſia (a ſalt very ſimilar to vitriolated natron) during ſolution in the diluted nitrous acid, produced nearly as much cold as that ſalt: the ſmall difference there is between them, as to this effect, may be owing to the former containing rather leſs water in its cryſtals.

Vitriolated natron, liquified by heat, was ſet to cool; when its temperature was reduced to 70°, it became ſolid, and the thermometer immediately roſe to 88° (eighteen degrees) its freezing point. Does not the quantity of ſenſible heat evolved by this ſalt, in becoming ſolid, indicate its great capacity for heat, in returning to a liquid ſtate, and conſequently account in a great meaſure for its producing ſuch intenſe cold during ſolution in the diluted mineral acids? Two ſalts, vitriolated argillaceous earth (alum) and tartarized natron (Rochelle ſalt), each contain nearly as much water of cryſtallization as vitriolated natron; but produced neither of them any conſiderable effect during ſolution in the diluted nitrous acid; the latter made the thermometer riſe: neither did their temperatures increaſe, like that ſalt, in changing from a liquid to a ſolid ſtate.

From the obvious application of artificial frigorific mixtures to uſeful purpoſes, in hot climates eſpecially, where the inhabitants ſcarcely know by the ſenſe of feeling winter from ſummer, it may not be amiſs to hint at the eaſieſt and moſt œconomical method of uſing them. For moſt intentions, perhaps, the following cheap one may be ſufficient: of ſtrong vitriolic acid, diluted with an equal weight of water, and cooled to the temperature of the air, any quantity; add to this an equal weight of vitriolated natron in powder: this is the proportion when the temperature ſet out with is + 50°, and will ſink the thermometer to 5°; if higher, the quantity of the ſalt muſt be proportionably increaſed. The obvious and beſt method of finding the neceſſary quantity of any ſalt to produce the greateſt effect, by ſolution in any liquid, at any given temperature, is by adding it gradually until the thermometer ceaſes to ſink, ſtirring the mixture all the while.

If a more intenſe cold be required, double aqua fortis, as it is called, may be uſed; vitriolated natron, in powder, added to this, produces very nearly as much cold as when added to the diluted nitrous acid: it requires a rather larger quantity of the ſalt, at the temperature of + 50°, about three parts of the ſalt to two parts of the acid: it will ſink the thermometer from that temperature nearly to 0, and the conſequence of more ſalt being required is, its retaining the cold rather longer. This mixture has one great recommendation, a ſaving of time and trouble. A little water in a phial, immerſed in a ſmall tea-cup of this mixture, will be ſoon frozen in ſummer; and if the ſalt be added in cryſtals unpounded to double aqua fortis, even at a warm temperature, the cold produced will be ſufficient to freeze water or creams; but if diluted with one-fifth its weight of water, and cooled, it is about equal to the diluted nitrous acid above mentioned, and requires the ſame proportion of the ſalt. A mixture of vitriolated natron and diluted nitrous acid ſunk the thermometer from + 70° (temperature of air and ingredients) to + 10°.

The cold in any of theſe mixtures may be kept up a long time by occaſional additions of the ingredients in the proportions mentioned. A chemiſt would make the ſame materials ſerve his purpoſe repeatedly.

Equal parts of muriated ammonia and nitrated kali in powder make a cheap and convenient compoſition for producing cold

cold by ſolution in water; it will, by the following manage-ment, freeze water or creams at Midſummer.

June 12th, 1787, a very hot day, I poured four ounces, wine meaſure, of pump-water, at the temperature of 50° (it is well known that water at ſprings retains nearly the ſame temperature winter and ſummer, *viz.* about 50°, to which temperature the water may be reduced during the warmeſt weather, by pumping off ſome firſt) upon three ounces, Avoirdupois weight, of the above powder (previouſly cooled by immerſing the veſſel containing it in other water at 50°), and after ſtirring the mixture its temperature was 14°; ſome water contained in a ſmall phial, immerſed in this mixture, was conſequently ſoon frozen. This ſolution was afterwards evaporated to dryneſs, in an earthen veſſel, reduced to powder, and added to the ſame quantity of water, under the ſame circumſtances as before, when it again ſunk the thermometer to 14°. Since that time I have repeatedly uſed a compoſition of this kind for the purpoſe of producing cold, without obſerving any diminution in its effect after many evaporations. The cold may be œconomically kept up and regulated any length of time, by occaſionally pouring off the clear ſaturated liquor, and adding freſh water, obſerving to ſupply it conſtantly with as much of the powder as it will diſſolve.

The degree of cold at which water begins to freeze has been obſerved to vary much; but that it might be cooled twenty-two degrees below its freezing point was perfectly unknown to me until lately. I filled the bulb of two thermometers, one with the pureſt rain-water I could procure, the other with pump water; the water was then made to boil in each, until one-third only remained: theſe were kept in a frigorific mixture, at the temperature of +10°, for a much longer time than

than I thought neceſſary to cool the water to the ſame temperature; and by repeated trials I found it was neceſſary to lower the temperature of the mixture to near $+5°$, to make the water in either of them freeze. Theſe were likewiſe ſuſpended out of doors, cloſe to a thermometer, during the late froſt, and the water never obſerved frozen. On March the 22d, at ſix in the morning, the water in each remained unfrozen, though the tubes were gently ſhaken, the thermometer ſtanding at that time at 23°. There appeared to be little difference with reſpect to the degree of cold neceſſary to freeze the water, whether the tube of the thermometers were open or cloſed in vacuo (which was very nearly effected by ſuffering the water to boil up to the orifice of the tube, and then ſuddenly ſealing it) or not, but unboiled water in the ſame ſituation froze in a higher temperature.

It is commonly ſuppoſed, I believe, that gentle agitation of any kind will diſpoſe water (cooled below its freezing point) to become ice; but I have repeatedly cooled rain-water and pump-water, boiled a long time, and unboiled, in open veſſels to 30° or lower, and have conſtantly ſucceeded, after trying other kinds of agitation in vain, by ſtirring, or rather ſcraping gently, the bottom and ſides of the veſſel containing the water to be frozen, when after ſome ſhort time ſmall filaments of ice appeared, and by continuing this motion about every part of the veſſel beneath the ſurface of the water, about two-thirds of the water commonly froze. A ſlender, pointed glaſs rod I uſed for this purpoſe.

I have the honour to be, &c.

RICH. WALKER.

Oxford, March 27, 1788.

Extract from a second Letter from Mr. Walker *to* Henry Cavendish, *Esq. Dated* Oxford, May 28, 1788.

A more intense cold may be produced by a solution of salts in water in summer, than can be produced by a mixture of snow and salt in winter. To rain-water six drachms (by weight) I added six drachms of nitrated ammonia reduced to a very fine powder which made the thermometer sink from +50° (temperature of the materials) to 4°, then adding six drachms of mineral alkali very finely powdered the thermometer sunk to −7°, fifty-seven degrees. It is observable, that in the latter there are two causes concur in producing the effect, the liquifaction both of the snow and salt; but in the experiment just mentioned the liquifaction of the salts only.

Vitriolated natron, after it had given out its water of crystallization by exposure to the atmosphere, produced no change of temperature by solution in the diluted nitrous acid, but during solution in water produced heat, as did likewise the mineral alkali.

I have since my last seen FAHRENHEIT's Experiments on the freezing of Water, related in Vol. XXXIII. of the Philosophical Transactions; but as mine differ in degree I take no farther notice of them.