XXV. *Experiments on the Congelation of the Vitriolic Acid. By* James Keir, *Eſq. F. R. S.; communicated by* Henry Cavendiſh, *Eſq. F. R. S.*

Read May 3, 1787.

THAT the vitriolic acid ſometimes aſſumes a ſolid, cryſtalline ſtate, has been obſerved by Basil Valentine, and by many later chemiſts; but their relations of this appearance are neither ſufficiently explicit, with regard to the eſſential and concomitant circumſtances, nor do they ſeem very conſiſtent with each other. It appears, however, that two very diſtinct ſpecies of congelation of this acid have been noticed. That which is deſcribed by the older chemiſts, and alſo by ſome modern authors, requires no greater degree of cold than the common temperature of the air, even in ſummer, and is peculiar to that acid which is obtained by diſtillation from martial vitriol, and which is poſſeſſed of a ſmoking quality in a high degree: for not only the authors, by whom this congelation has been obſerved, have given this deſcription of the acid employed, but alſo the late experiments of M. Dollfuss * ſeem to ſhew, that the ſmoking quality is eſſential to the phænomenon; for neither the acid obtained from vitriol, when deprived by rectification of its ſmoking quality, nor the Engliſh oil of vitriol (which is known to be obtained by burning ſulphur, and

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* Crell Annalen 1785.

which

which does not ſmoke), were found, by his trials, to be ſuſceptible of this ſpecies of congelation. The acid, thus congealed, has been called *glacial*, or *icy oil of vitriol.*

The other kind of congelation has been little noticed till lately. To this congelation every kind of vitriolic acid is ſubject, whether it ſmokes or not, and whether it has been prepared from martial vitriol, or from ſulphur, provided the cold to which it is expoſed be ſufficiently intenſe: for the cold, requiſite for this ſpecies of congelation, is conſiderably greater than what is ſufficient for the former.

Mr. MACQUER relates, in the ſecond edition of his Dictionary of Chemiſtry *, that the Duke D'AYEN had obſerved the congelation of concentrated vitriolic acid, which had been expoſed to a cold expreſſed by 13 or 14 degrees below 0 of REAUMUR's ſcale; but that mixtures, conſiſting of one part of the above-mentioned concentrated acid, with two or more parts of water, could not be frozen by the cold to which he expoſed them, till he had diluted the acid ſo much, that its denſity was to that of water as 104½ to 96; in which latter caſe of congelation, it is probable, that the water only did freeze, as it does in dilute ſolutions of neutral ſalts. M. DE MORVEAU † has made ſimilar experiments, with a view to verify thoſe of the Duke D'AYEN, and with ſimilar ſucceſs. By means of an intenſe cold, produced by adding ſpirit of nitre to pounded ice, he congealed a part of ſome vitriolic acid, which he had previouſly concentrated. He obſerved, that although a very intenſe cold had been employed to freeze the concentrated acid, it nevertheleſs remained congealed in much leſs degrees of cold, and that it thawed very ſlowly. Laſtly, ſome experiments have

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* Article, Vitriolic Acid.

† Mem. de l'Acad. de Dijon, pour 1782.

have lately been made by Mr. M^c^ NAB, at Hudſon's Bay, on the congelation of acids by intenſe cold; an account of which experiments is given in the Philoſophical Tranſactions for 1786, by Mr. CAVENDISH, at whoſe deſire they had been made. Theſe experiments are the more valuable, as the denſity of the acids employed, and the temperature, and other concomitant circumſtances, have been diſtinctly noted; and they are rendered ſtill more intereſting, by the very judicious remarks made on them by Mr. CAVENDISH. It is there related, that a vitriolic acid, whoſe ſpecific gravity was to that of water as 1843.7 to 1000, froze when expoſed to a cold of − 15° of FAHRENHEIT's ſcale; that another more dilute vitriolic acid, conſiſting of 629 parts of the former concentrated acid, and 351 parts of water, congealed in a temperature of − 36°; and that when the acid was further diluted, it was found capable of ſuſtaining a much greater cold without freezing. In theſe experiments, as alſo in thoſe of M. DE MORVEAU, it appeared, that the whole of the acid did not congeal, but that part of it retained its fluidity. Mr. CAVENDISH found, on examining the part which had congealed, and that which had remained fluid, that they were *nearly* of the ſame ſtrength; and he is thence led to think, that the difference between them, by which the one is more diſpoſed to congeal than the other, does not depend on their different ſtrengths, but on ſome quality leſs obvious, and the ſame which conſtitutes the difference between glacial and common oil of vitriol. In all the experiments which had been made by the Duke D'AYEN, M. DE MORVEAU, and Mr. M^c^ NAB, the vitriolic acid, when ſtrong, had frozen with leſs cold than when diluted; but theſe experiments did not enable Mr. CAVENDISH to determine, whether this acid has any determinate ſtrength or *point of eaſieſt freezing* (ſuch as he had diſcovered to be poſſeſſed by ſpirit of nitre), or whether the cold requiſite for congelation does not continually diminiſh, as the ſtrength of the acid increaſes, without limitation. This latter opinion he thinks the moſt probable, from the circumſtance of the Duke D'AYEN's and M. DE MORVEAU's acids having frozen with a conſiderably leſs intenſe cold than thoſe of Mr. M^c^ NAB, which, he ſuppoſes, were weaker, as the former acids had been concentrated purpoſely.

The obſervations which I have made, and am going to relate, apply ſolely to the latter kind of congelation of the vitriolic acid, as the acid which I employed was of the kind that is prepared by burning ſulphur, and is commonly ſold in England under the name of oil of vitriol, and was perfectly free from colour, ſmell, or ſmoking quality. After a ſevere froſt at the end of the year 1784, and beginning of 1785, I obſerved that ſome vitriolic acid, contained in a corked phial, had congealed; while other parcels of the ſame acid, ſome ſtronger and ſome weaker, equally expoſed to the cold, had remained fluid. As I imputed the congelation to the great intenſity of the cold, I was afterwards much ſurpriſed, when the froſt ceaſed, to find that the acid remained frozen during many days, when the temperature of the air was ſometimes above 40° of FAHRENHEIT's ſcale; and when the congealed acid was brought into a warm room, purpoſely to thaw it, a thermometer, placed in contact with it during its thawing, continued ſtationary at 45°. From theſe circumſtances I concluded, that the freezing and thawing point of this acid was very near the laſt mentioned degree; and, accordingly, upon expoſing the liquor which had been thawed to the air, at the temperature of 30°, the congelation again took place in a few hours. From the circumſtance of other parcels of the ſame acid, but of different ſtrengths, remaining fluid, although they had been expoſed to a much greater cold than was neceſſary for the congelation of that acid liquor which had frozen, I was led to believe, that there muſt be ſome certain ſtrength at which the vitriolic acid was more diſpoſed to freeze than at any other, greater or leſs. I knew that the ſpecific gravity of the acid which had frozen was nearly to that of water as 1800 to 1000, and that of the ſtronger acid, which had not frozen, was as 1846 to 1000; which laſt is the uſual denſity of the oil of vitriol commonly ſold in England. I knew alſo, that the acid which had frozen was in no reſpect but in ſtrength different from the ſtronger acid which had retained its fluidity; having myſelf, ſome weeks before, taken the former acid from the bottle containing the latter, and diluted it with water till it was reduced to the ſpecific gravity of 1800.

Although from the above obſervations I was convinced of the propoſition generally, that the vitriolic acid is moſt diſpoſed to freeze when at a certain ſtrength, and then it is ſuſceptible of congelation by means of much leſs cold than has been hitherto imagined; yet, as only part of my acid had frozen, I could not with certainty know the ſtrength of the frozen part, and I therefore was not able to ſtate, with any accuracy, the degree of ſtrength moſt favourable to congelation, nor the limits of ſtrength within which the acid may be congealed by ſuch moderate cold. In the following winter I had not leiſure to purſue the ſubject; but ſince the commencement of the preſent year, I have verified my former obſervation with more attention to the exact denſities of the acids; and I have found, that the point of ſtrength moſt favourable to congelation is very determinate, and that a very ſmall variation above or below that point renders the acid incapable of freezing without a conſiderable augmentation of cold. As the acid,

acid, when brought to the proper ſtrength, was capable of freezing with leſs cold than water does, I immerſed ſeveral acids of different ſtrengths in melting ſnow, inſtead of expoſing them to the air, the temperature of which was variable, whereas that of melting ſnow was conſtant and determinate. Thoſe acids which would not freeze in melting ſnow, were afterwards immerſed in a mixture of ſnow, water, and common ſalt, the temperature of which was not ſo conſtant and determinate as that of melting ſnow; but it generally remained for ſeveral hours at about 18°, and was ſometimes ſeveral degrees lower. The intention of adding water to the ſnow and ſalt was to leſſen the intenſity of the cold of this mixture, and to render it more permanent than if the ſnow and ſalt alone were mixed.

The acids which had frozen in melting ſnow, and which were five in number, having been thawed and brought to the temperature of 60°, were found on examination to have the following ſpecific gravities.

1786
1784
1780
1778
1775

Thoſe acids which would not freeze in melting ſnow, but which froze when immerſed in ſnow, water, and ſalt, having been expoſed to a greater cold, were of a greater latitude of denſity. Their ſpecific gravities, when brought to the temperature of 60°, were found to be expreſſed by the following numbers.

1814
1810

1804
1794
1790
1770
1759
1750

The acids which remained, and which would not freeze either in melting ſnow, or in the mixture of ſnow, ſalt, and water, were found on examination to have the following ſpecific gravities.

1846
1839
1815
1745
1720
1700
1610
1551

It appears, from the firſt table of ſpecific gravities, that the medium denſity of the acids which did freeze with the cold of melting ſnow was 1780; and from the ſecond table it appears, that, at the denſities of 1790 and 1770, the acid had been incapable of freezing with that degree of cold. Hence it follows, that 1780 is nearly the ſtrength or denſity of eaſieſt freezing; and that an increaſe or diminution of that denſity, equal to $\frac{1}{178}$th part, renders the acid incapable of freezing with the cold of melting ſnow, notwithſtanding this cold is ſome degrees above the freezing point of the moſt congelable acid. From the ſecond table of ſpecific gravities it appears, that by applying a more intenſe cold, namely, that produced by a mixture of ſnow, ſalt, and water, the limits of the denſity of the acids capable of congelation were extended to about $\frac{3}{178}$ above or below the point of eaſieſt freezing: and there ſeems

ſeems little reaſon to doubt, that, by greater augmentations of cold, theſe limits may be further extended; but in what ratio theſe augmentations and extenſions proceed cannot be determined without many obſervations made in different temperatures.

Although it is probable, that the moſt concentrated acids may be frozen, provided the cold be ſufficiently intenſe, yet there ſeems to me reaſon to believe, that ſome of the congelations which have been obſerved in highly concentrated acids have been effected in conſequence of the denſity of theſe acids having been reduced nearly to the point of eaſy freezing by their having abſorbed moiſture from the air: for the Duke D'AYEN and M. DE MORVEAU expoſed their acids to the air, in cups or open veſſels; and the latter author even acquaints us, that, on examining the ſpecific gravity of the acid which had frozen, he found it to be to that of water as 129 to 74; which denſity being leſs than the point of eaſieſt freezing, proves that the acid which he employed, and which he had previouſly concentrated, had actually been weakened during the experiment. I have ſeveral times expoſed concentrated oil of vitriol in open veſſels in froſty weather; and I have ſometimes, but not always, obſerved a congelation take place. Upon ſeparating the fluid from the congealed part, and upon examining the ſpecific gravity of the latter, after it had thawed, I found that it had been reduced to the ſtandard of eaſieſt freezing. When the congealed acid was kept longer expoſed, it gradually thawed, even when the cold of the air increaſed; the reaſon of which is not to be imputed to the heat produced by the moiſture of the air mixing with the acid, for this cauſe operated during the congelation, but principally to the diminution of denſity below the point of eaſy freezing, which was occaſioned by the continued abſorption of moiſture from the air, and which rendered

rendered the acid incapable of continuing frozen without a great increaſe of cold.

It appears then, that the concentration of M. DE MORVEAU's acid, at the time of its congelation, from which circumſtance Mr. CAVENDISH infers generally, that the vitriolic acid freezes more eaſily as it is more denſe, is not a true premiſe; and that therefore the inference, though juſtly deduced, is invalid. On the contrary, there ſeems every reaſon to believe, from the analogy of my experiments above mentioned, that as the denſity of the acid increaſes beyond the point of eaſieſt freezing, the facility of the congelation diminiſhes; at leaſt, to as great denſity as we have been ever able to obtain the vitriolic acid; for if it were poſſible to diveſt it intirely of water, it would probably aſſume a ſolid ſtate in any temperature of the air.

The cryſtallization of the frozen vitriolic acid is more or leſs diſtinct, according to the ſlowneſs of its formation, and other favourable circumſtances. Sometimes the cryſtals are very diſtinctly ſhaped, large, and very hard. Their form is the ſame as the common form of mineral alkali and of ſelenitic ſpar, but with angles different in dimenſions from either of theſe. They are ſolids conſiſting of ten faces, of which the two largeſt are equal, parallel, and oppoſite to each other, and are oblique-angled parallelograms or rhomboids, whoſe angles are, as near as I could meaſure them, of 105 and 75 degrees. Between theſe two rhomboidal faces are placed eight faces of the form of trapeziums. Thus each cryſtal may be ſuppoſed to be compoſed of two equal and ſimilar fruſtums of pyramids joined together by their rhomboidal baſes. I obſerved, that the cryſtals always ſunk in the fluid acid to the bottom of the veſſel, which ſhewed that their denſity was increaſed by congelation.

I thought

I thought of aſcertaining their ſpecific gravity by adding gradually to this fluid part ſome concentrated vitriolic acid, till the cryſtals ſhould float in the liquor, the examination of whoſe ſpecific gravity would determine that of the floating cryſtals. But I was ſurpriſed to find, that the cryſtals ſunk even in the concentrated acid, and conſequently were denſer. I then poured ſome of the congelable acid, previouſly brought to the freezing temperature, into a graduated narrow cylindrical glaſs, up to a certain mark, which indicated a ſpace equal to that occupied by 200 grains of water. The glaſs was placed in a mixture of ſnow, ſalt, and water, and when the acid was frozen, a mark was made on the part of the glaſs to which the acid had ſunk. Having thawed the acid, and emptied the glaſs, I filled it with water to the mark to which the acid had ſunk by freezing, and I found, that fifteen grains more of water were required to raiſe it to the mark expreſſing 200 grains; which ſhews, that the diminution of bulk, ſuſtained by the acid in freezing, had been equal to $\frac{1}{13.3}$ of the whole.

Computing from this *datum*, we ſhould eſtimate the ſpecific gravity of the congealed acid to have been 1924; but as it contained evidently a great number of bubbles, its real ſpecific gravity muſt be conſiderably greater than the above determination, and cannot eaſily be aſcertained on account of theſe bubbles. By way of compariſon, I obſerved the alteration of bulk which water contained in the ſame cylindrical glaſs would ſuffer by freezing; and I found that its expanſion was equal to about $\frac{1}{10}$th part of its bulk. The water had been previouſly boiled; but it nevertheleſs contained numberleſs bubbles. In this reſpect then there is a remarkable difference between the congelations of water and of vitriolic acid; but, perhaps, the difference

difference ariſes principally from the bubbles of elaſtic fluid, which may be in greater quantity, and may add more to the bulk of the water than of the acid.

Greater cold is produced by mixing ſnow or pounded ice with the congealed than with the fluid acid, but the quantity I have not determined. There is reaſon to believe it may be conſiderable. In the experiments made at Hudſon's Bay, by Mr. M^c^ NAB, the greateſt cold which he had produced by mixing acids with ſnow, was effected by a vitriolic acid which had previouſly congealed; and to this circumſtance of the congelation of the acid, Mr. CAVENDISH juſtly imputes the intenſity of the cold, as the liquefaction of both the frozen acid and the ſnow had concurred towards this effect; whereas, in mixing fluid acids with ſnow, the thawing of the ſnow is probably the ſole productive cauſe.

I was deſirous of comparing the times required for the liquefaction of ice and of congealed acid, when both were expoſed to the ſame temperature. For this purpoſe I filled two equal and ſimilar cylindrical glaſſes; one with the congelable vitriolic acid, and the other with water; and, after having immerſed them in a freezing mixture till both fluids were frozen, and reduced to the temperature of 28°, I withdrew the glaſſes from the freezing mixture, wiped them dry, and placed them together in a room, where the thermometer ſtood at 62°. In 40 minutes the ice was thawed, and in 95 minutes the acid was liquefied, at the end of which time the thermometer, which ſtood near the glaſſes, had riſen to 64°. It appears then, that the congealed acid requires more than twice the time for its liquefaction, when expoſed to that temperature, that ice does; but I do not think that we can infer, that the heats abſorbed and rendered *latent*, as ſome late philoſophers expreſs themſelves; or, in other words, that the cold generated by the liquefaction of ice and of congealed acid are in the above proportion of the times, from the following conſideration; that, as during the liquefaction of the ice, its temperature remains ſtationary at 32°, and during the liquefaction of the acid, its temperature remains about 44° or 45°, the ice, being conſiderably colder than the acid, will take the heat from the contiguous air much faſter.

The experiment does however ſhew, that a conſiderable quantity of cold is generated by the liquefaction of this acid; and hence it appears probable, that in making experiments of producing cold artificially, by mixing ſnow with acids in very cold temperatures, it would probably be uſeful to employ a vitriolic acid of the proper denſity for congelation, and to freeze it previouſly to its mixture with ſnow.

It muſt not, however, be imagined, that the cold generated by the mixture of theſe two frozen ſubſtances is nearly equal to the ſums of the colds generated by the ſeparate liquefactions of the congealed acid and ice, when ſingly expoſed to a thawing temperature: for the mixture reſulting from the liquefaction, conſiſting of the vitriolic acid and the water of the ſnow, appears, from the generation of heat which occurs in the mixture of theſe ingredients in a fluid ſtate, to be ſubject to different laws relatively to heat, than either of the ingredients ſeparately. And the heat, thus generated, as ſoon as the congealed acid and ice are brought to a fluid ſtate, muſt counteract, in ſome meaſure, the cold produced by the liquefaction.

The vitriolic acid, like water and other fluids, is capable of retaining its fluidity when cooled conſiderably below its freezing point. I placed a phial, containing ſome congelable vitriolic

vitriolic acid, in a mixture of ſalt, ſnow, and water; and ſoon afterwards, while the acid was yet fluid, I immerſed in it a thermometer, the mercury of which quickly ſunk from 50° to 29°. While I was moving the thermometer in the fluid, in order to make it acquire the exact temperature, I ſaw the mercury ſuddenly riſe, and upon looking at the acid, I obſerved numberleſs ſmall cryſtals floating in it, which had been ſuddenly formed. The degree to which the mercury then roſe was 46°½. Another time, while the acid was freezing, the thermometer placed in it ſtood at 45°.

From the above obſervations, the following inferences may be drawn.

1ſt, That the vitriolic acid has *a point of eaſieſt freezing*; that is, there is a certain ſtrength or denſity, at which this acid freezes with conſiderably leſs cold than at any other ſtrength, greater or leſs; and that this denſity is nearly to that of water as 1780 is to 1000.

2dly, That the greater or leſs diſpoſition of congelation of the vitriolic acid, which is free from the ſmoking quality that is peculiar to the acid obtained by diſtilling martial vitriol, does not depend on any other quality or circumſtance than its ſtrength or denſity.

3dly, That the freezing and thawing degree of the moſt congelable acid is about 45° of FAHRENHEIT's ſcale. It is, however, to be obſerved, that this degree is inferred from the temperature indicated by the thermometers immerſed in the freezing and thawing acids; but that I never effected the congelation of the fluid acid, without expoſing it to a greater cold, namely, either that of melting ſnow, or of the external air in froſty weather.

Like water, this acid poſſeſſes the property of retaining its fluidity when cooled ſeveral degrees below its freezing point; and of riſing ſuddenly to this point, when its congelation is promoted by agitation, or by contact with even a warmer thermometer.

4thly, That, like water and other congelable fluids, the vitriolic acid generates cold during its liquefaction, and heat during its congelation; the quantity of which heat and cold, ſo generated, remains to be determined by future experiments.

5thly, That the acid, by congelation, when the circumſtances for diſtinct cryſtallization are favourable, aſſumes a regular cryſtalline form, a conſiderable ſolidity and hardneſs, and a denſity much greater than it poſſeſſed in a fluid ſtate.

With reſpect to the firſt mentioned ſpecies of congelation, which is peculiar to the ſmoking vitriolic acid that is procured from martial vitriol, although I have had no opportunity of ſeeing it, as all the vitriolic acid, that is uſed in this country, is obtained by burning ſulphur, yet I will beg leave to ſuggeſt, that it may be worth the attention of thoſe chemiſts to whom it occurs, to obſerve more accurately than has been done, the freezing temperature and the denſity of the congelable acids; and to examine whether the denſity of this ſmoking acid alſo is connected with the glacial property. It ſeems further to be deſerving of inveſtigation, whether there is not ſome analogy between the congelation of the ſmoking oil of vitriol, and the very curious cryſtallization which Dr. PRIESTLEY obſerved in a concentrated vitriolic acid, ſaturated with nitrous acid vapours *; and whether this ſmoking quality does

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* Experiments and Obſervations relating to various Branches of Natural Philoſophy.

does not proceed from ſome marine or other volatile acid, which may be contained in the martial vitriol, whence the vitriolic acid is obtained.

Philoſophy, vol. I. p. 26. and 450. M. CORNETTE has alſo effected the cryſtallization of vitriolic acid by diſtilling it with nitrous acid and charcoal. Memoir. de l'Acad. des Scienc. Paris, pour 1779.