

ON THE  
RELATIVE ATTRACTIONS  
OF  
SULPHURIC ACID FOR WATER,

*Under particular circumstances :*

WITH SUGGESTION OF MEANS OF IMPROVING THE  
ORDINARY PROCESS OF MANUFACTURING  
SULPHURIC ACID.

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(Read 16th of April, 1839.)

THOUGH it has been long known that concentrated sulphuric acid, in consequence of its great attraction for water, robs the atmosphere of its vapour, and becomes thereby itself diluted; and though its drying agency is frequently adverted to in our laboratories in cases of research, where drying by the application of heat would be objectionable; I do not know that any person has hitherto attempted to trace out by experiment the limits within which the acid in question is a drier of the atmosphere. Works on chemistry



give us no information on the subject ; but, from some of them, we learn that experiments have been made on the extent to which the acid becomes diluted by exposure to the atmosphere ; these experiments, however, being so limited in their nature as to fall far short of eliciting that information which it has seemed to me desirable for us to possess. In Dr. Ure's Dictionary we are told that, if suffered to remain in an open vessel, it imbibes one-third of its weight in 24 hours, and more than six times its weight in a twelve month. And in Dr. Thomson's System of Chemistry we are told that Newman found, that, when exposed to the atmosphere, it attracted 6.25 times its own weight ; and that Mr. Gould found that 180 grains of it, when exposed to the atmosphere, attracted 68 grains of water the first day, 58 the second, 39 the third, 23 the fourth, 18 the fifth, and at last only 5, 4, 3, &c. ; the 28th day the augmentation was only half a grain. We are not informed in what state of dryness the atmosphere was during these exposures, nor have we anything beyond evidence that sulphuric acid has a strong attraction for water.

In the course of some experiments which I was some time ago conducting to ascertain the



per centages of water in the crystals of some soda salts, by submitting them to the drying agency of a vacuum accompanied by a vessel of sulphuric acid, the results of which were communicated to this Society, I frequently felt at a loss to know whether the acid I had under the receiver was sufficiently strong to render the space perfectly anhydrous ; or, indeed, to render it sufficiently dry to deprive the salts under operation of as much water as anhydrous space could do ; and, consequently, I much more frequently renewed the acid than was really requisite. The annoyance of doubt, thus frequently felt in impairing that spirit of confidence which always ought to accompany philosophical investigation, proved itself a stimulus to subsequent experimental inquiry, the result whereof furnishes us with facts on which we may, I hope, rely in after research ; and adds, though little, in assisting to fill up the vast hiatus remaining to be filled up before our knowledge of Nature's laws can be said to be complete.

The object of my inquiry was, to determine at what degree of concentration the affinity of sulphuric acid for aqueous vapour is equal to that of anhydrous space for the same vapour at particu-



lar temperatures. To effect this object, the experiments which I now commence relating were undertaken.

## EXPERIMENT I.

I put into a glass evaporating dish of known weight 200 grains of sulphuric acid, sp. gr. about 1.8428; and then intimately mixed therewith a little water, by which considerable heat was produced.\* After the dish and contents had been cooled by immersion for a short time in cold water, it was found, by weighing, that the quantity of water which I had added was 15 grains. Into another similar dish I put 200 grains of the acid, but did not add thereto any water. Both dishes were then immediately placed under an exhausted air-pump receiver. On the following day I re-weighed them, and found that the one into which the 15 grains of water had been put had gained 0.6 of a grain, and the other 1.2

\* It may be proper to observe, that the acid I used throughout my experiments was some which a friend of mine, Mr. H. Blair, an extensive manufacturer of the article, prepared for me with more than ordinary care. I found, by evaporation, that its total impurity amounted only to the 1-20th of one per cent. And 100 grains gave with nitrate of barytes 233 grains of sulphate, = 79 real, or anhydrous sulphuric acid.



grain. This additional water must have been acquired from the atmosphere while the dishes were in being transferred to and from the receiver.

It being evident that the undiluted acid had not taken from the diluted acid any of its water, I now added to the diluted acid 9.3 grains more water; and, with the same precautions as to cooling as before, placed both dishes again under the exhausted receiver. In a few days they were re-weighed, when the diluted acid was found to have lost 1.1 grain, and the undiluted to have gained it. Both were again put under the receiver, and by several times weighing and replacing them there, the diluted acid was found to lose weight, until the total loss was 1.9 grain. Had the experiment been continued, a little further loss would have been sustained; but being able to guess, as I imagined, from what had already taken place, to about the extent to which concentrated acid would bear diluting, without having its affinity for water so much diminished as to be compelled to yield to the attractive agency of anhydrous space, I resolved upon recommencing the experiment; and, consequently, on the 22d September, 1837, I put into one dish



200 grains of the acid, sp. gr. 1.8428, diluted in the manner described before, with 23.3 grains of water (23 grains being the quantity with which the 200 grains of acid were in a state of dilution at the conclusion of the experiment in the other instance,) and into another dish 200 grains of the acid without being diluted. Both dishes were kept under the exhausted receiver as before. On the 29th September the diluted acid was found to have lost 1.3 grain; on the 6th October, 1.7 grain; and on the 13th, 2.4 grains: on the 20th and 27th, the weight was exactly the same as on the 13th; the concentration being evidently carried to as high a degree as the evaporating agency of anhydrous space, under the circumstances of the case, would admit of.

Now, by deducting 2.4 from 23.3, we find that the quantity of water which the 200 grains of concentrated acid retained is 20.9 grains, or that 100 grains of the acid retained 10.45 grains of the water added. Admitting that the concentrated acid contained 79 per cent. real, it must also have contained 21 per cent. of water:—we then have  $21 + 10.45 = 31.45$  the total quantity of water diluting 79 real acid at the conclusion of the experiment; and  $79 + 31.45 = 110.45$  the



total quantity of diluted acid remaining in the dish; the per centage of real acid in which being 71.53 nearly; acid of this strength is of about the sp. gr. 1.814.

The temperature of that particular part of the room in which this air pump experiment was made, was regularly registered three times a day, whereby it was perceived that from the 22nd September to the 6th October, the temperature never ran higher than  $65^{\circ}$ , and from the 6th October to the 13th, not higher than  $57^{\circ}$ ; from the 13th to the 27th, it was also frequently as high as  $57^{\circ}$ ; hence it follows, that an evaporating force of 0.61 of an inch of mercury, has, in the instance of this experiment, been sufficient to concentrate the acid down to the sp. gr. 1.814; and, consequently, that acid of such strength is capable of drying a vacuum when the temperature does not exceed  $57^{\circ}$ .

#### EXPERIMENT II.

On the morning of the 3rd October, 1837, I put into two light evaporating dishes, of  $2\frac{1}{4}$  inches in diameter, 10 grains by weight of diluted sulphuric acid, sp. gr. 1.135; and the dishes, after being moved about until the acid had spread itself



over the whole surface of the bottoms, were left exposed to the atmosphere in a room without fire. They were re-weighed every morning during the continuance of the experiment, and several times moved about every day to agitate the contents. The temperature and vapour point of the room were accurately ascertained, and registered three times a day.\* On the 4th October, each dish was found to have lost 3.2 grains, and on the 5th 4.3 grains; on the 6th each was found to have regained 0.2 of a grain, and on the 7th their weights were exactly the same as on the 6th. In each case, therefore, the weight of the diluted acid on the 6th and 7th, was 4.1 grains less than when put into the dish. The loss of water was 41 per cent; the liquid remaining in each dish being 5.9 grains. If we suppose 100 grains of the diluted acid to have been used in this experiment instead of 10, they would have been reduced to 59 grains, those 59 grains containing all the anhydrous sulphuric acid which was in the 100 grains of the diluted acid experimented upon, viz. 15.8 grains;† the per centage, therefore, of

\* The vapour point was ascertained by Dr. Dalton's method.

† By treating 100 grains of this diluted acid with nitrate of barytes, I obtained 46.7 grains of sulphate, = 15.8 anhydrous sulphuric acid.



anhydrous acid in the 59 grains remaining in the dish, being nearly 26.78.

In order to understand the state of the atmosphere during the experiment, it is necessary to appeal to the register of the temperature, and vapour point, of which the following is a copy.

1837. Oct.	TEMPERATURE.			VAPOUR POINT.		
	Morn.	Noon.	Night.	Morn.	Noon.	Night.
3	61°	63°	64°	53°	55°	56°
4	64	65	63	56	56	53
5	59	63	62	50	54	53
6	63	63	62	54	54	53
7	60	62	62	51	53	53
8	62	62	61	53	54	52

The annexed table shows the evaporating force of the atmosphere, or the affinity of space for vapour, as ascertained by deducting the force of vapour at the temperature of the vapour point from its force at the temperature of the atmosphere; the forces of vapour at the respective temperatures being taken from the table in the second volume of Dr. Dalton's New System of Chemistry; and which, as I have frequently to refer to it, I have copied into a subsequent part of this paper.



1837.	EVAPORATING FORCE.		
Oct.	Morn.	Noon.	Night.
	Inch of Mer.	Inch of Mer.	Inch of Mer.
3	0.13	0.13	0.14
4	0.14	0.16	0.17
5	0.15	0.15	0.15
6	0.15	0.15	0.15
7	0.15	0.15	0.15
8	0.15	0.13	0.15

On comparing the results of the several weighings with this register of evaporating force, we observe that weight was found to be lost till and on the morning of the 5th, and that from the commencement of the experiment to that time the evaporating force had ranged from 0.13 of an inch of mercury to 0.17 of an inch. We also observe that on the morning of the 6th a slight regain of weight was found; and that from the morning of the 5th to that of the 6th the evaporating force had all the time been stationary at 0.15 of an inch of mercury. Up to the night of the 4th the acid had become concentrated to such a degree as that it was capable of resisting an evaporating force of 0.16 or 0.17 of an inch of mercury; and when the evaporating force happened to be reduced on the 5th to 0.15 of an inch, the acid was so far capable of overcoming that force as to regain 0.2 of a grain, and to retain that on the 6th, and as long as the evaporating force remained as then.



I have stated, that on the 6th and 7th the concentration of the acid had extended so far as to cause the per centage of real, or anhydrous, acid in the residue in the dish to be about 26.78 ; acid of such strength is of about the sp. gr. 1.249. Hence, it follows that when the affinity of space for vapour, or the evaporating force, is equal to 0.15 of an inch of mercury, it is just able to balance the affinity of sulphuric acid sp. gr. 1.249 (or such at least as contains 26.78 per cent. of real) for water.

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It is well known that ordinary evaporation from water goes on at a greater *rate* in vacuo than in air under atmospheric pressure ; and it might obviously be expected that the rate at which water would evaporate from diluted sulphuric acid would be greater in vacuo than in air ; but, at the conclusion of the experiments I have related, it seemed to be matter worth investigation to ascertain whether the evaporation of water from diluted sulphuric acid was capable of being carried on to the same *extent* in air as in vacuo ; or, in other words, whether the same strength of acid was required to render air at its usual pres-



sure anhydrous, as was required to render a vacuum of the same temperature anhydrous. And, accordingly, on the 1st of November, 1837, I commenced two comparative experiments, with the view of acquiring this desirable information.

#### EXPERIMENTS III. AND IV.

Into one light evaporating dish of  $2\frac{3}{4}$  inches in diameter I put 200 grains of the sulphuric acid, sp. gr. 1.8428, and diluted it with 24 grains of water, (attending to the precautions mentioned in the instances of the former experiments). The dish, with its contents, was then placed upon an air-pump plate, along with another glass vessel of an equal diameter, containing several hundred grains of the concentrated acid, and covered with a receiver, which was immediately exhausted as much as the capability of the pump would allow.

Into another light dish of the same diameter I also put 200 grains of the acid, sp. gr. 1.8428, which I diluted with 24.2 grains of water. This dish, with its contents, was placed upon a ground brass plate, similar to that of the air-pump, along with another glass vessel of an equal diameter, containing several hundred grains of the concentrated acid, and covered with an air-pump receiver,



tallowed to prevent the passage of air, *but not exhausted*. This brass plate supporting the unexhausted receiver, was placed in the immediate neighbourhood of the air pump, so as to ensure the exposure of the two experiments to the very same temperatures.

In these states, the dishes, the objects of experiment, were kept till the 8th November, when that under the exhausted receiver, was found, by weighing, neither to have gained nor lost the slightest weight ; but that under the unexhausted receiver, was found to be 0.7 grain heavier than at the commencement of the experiment. It being evident that the acid, in neither case, was sufficiently diluted to allow either a vacuum or dry air to rob it of any water at the temperatures it had been subjected to, the dilution was carried further. The acid in the dish under the exhausted receiver, had water added to it until the total quantity of water diluting the 200 grains of concentrated acid was 76.1 grains ; and that in the dish under the unexhausted receiver, had water added till the total quantity diluting the 200 grains of concentrated acid was 75.5 grains : both dishes being placed under their respective receivers, were kept there, as before, till the 15th



November, when the one under the exhausted receiver was found to have lost 30.6 grains, while that under the unexhausted receiver had only lost 4 grains. Both experiments were continued, and the losses of weight afterwards found to be as follows :—

1837.	Total loss from the dish under the exhausted receiver.	Total loss from the dish under the unexhaust- ed receiver.	Range of temperature to which the dishes, the ob- jects of experiment, were exposed between the pre- sent and next previous weighing.
	Grains.	Grains.	
Nov. 22	37.9	6.9	From 44° to 48°
“ 29	42.4	9.9	45 to 53
Dec. 6	44.9	11.9	43 to 48
“ 13	46.0	13.3	43 to 45
“ 20	46.9	14.8	44 to 53
“ 27	48.1	16.4	49 to 54
1838.			
Jan. 3	49.2	17.4	49 to 53
“ 10	50.0	18.4	39 to 49
“ 17	50.2	19.1	34 to 39
“ 24	50.2	19.2	34 to 39
“ 31	50.5	20.1	42 to 47
Feb. 7	50.6	20.8	42 to 44
“ 14	50.8	21.4	42 to 44
“ 23	51.5	22.4	40 to 46
March 2	51.6	22.7	42 to 46
“ 9	51.9	22.9	46 to 49
“ 16	52.3	23.3	48 to 53
“ 23	52.6	23.8	46 to 48
“ 30	52.6	23.8	45 to 48

As I could not, on the 30th March, detect any loss of weight to have taken place in either experiment, between then and the 23d, and as the



temperature had during the greater part of that interval been  $48^{\circ}$  (the maximum temperature of the previous week's interval,) I conclude that the acid the subject of each experiment, had become concentrated to as high a degree as it was capable of being, under the circumstances, and by no higher a temperature than  $48^{\circ}$ .

Then,  $76.1 - 52.6 = 23.5$  grains of water diluting the 200 grains of concentrated acid (sp. gr. 1.8428,) at the conclusion of the experiment under the exhausted receiver. And,  $75.5 - 23.8 = 51.7$  grains of water diluting the 200 grains of concentrated acid, at the conclusion of the experiment under the unexhausted receiver.—The acid in the dish under the exhausted receiver, was, therefore, so far concentrated as to contain 70.69 anhydrous acid per cent.; and that in the dish under the unexhausted receiver, 62.77 per cent.

It appears, from the results of these experiments, that weaker acid is required to render atmospheric air, at its usual pressure, anhydrous, than what is required to render a vacuum, of the same temperature, anhydrous; or, that the evaporating force of air, exerted upon diluted sulphuric acid, is less than that of a vacuum



of the same temperature. In opposition however, to this conclusion may perhaps be urged the apparent probability that the *air* was never, during the whole course of the experiment, rendered *really anhydrous*; that the concentrated acid might be incapable of depriving it of *all* its water, though it might be able to take some from it, and thereby give it a drying power great enough to cause it slowly to take water from the diluted acid, until the latter had acquired that degree of concentration which it was found to be of at the end of the experiment: but, bearing in mind that the maximum temperature to which the experiment was exposed, from the 23d to the 30th March, was such as would have been expected to give the space, if anhydrous, occupied by the air, a drying power equal to 0.46 of an inch of mercury, the experiments which I shall now mention will, I think, sufficiently show, that the concentrated acid was capable of depriving the air, or the space it occupied, of all its water, and of giving it the extreme evaporating force its temperature would admit of.

## EXPERIMENT V.

I diluted 100 grains of the concentrated acid, sp. gr. 1.8428, in a dish of  $2\frac{1}{4}$  inches in diameter,



with 15.2 grains of water, and left it, along with undiluted acid in another dish, under an unexhausted receiver (no larger than just requisite to cover the two dishes) standing in a plate of oil, from the 12th February, 1838, to the 22nd March, exposed to a temperature ranging each day as high as  $65^{\circ}$ , sometimes as high as  $77^{\circ}$ , and never lower than  $50^{\circ}$ ; during this time, the diluted acid lost no weight. Now, the maximum evaporating force of the temperature to which the acid in this experiment was subjected, was equal to 1.06 inch of mercury; and yet the acid lost by its action no water, though in a more dilute state than acid concentrated to the utmost under an exhausted receiver at the temperature of  $48^{\circ}$ , or with an evaporating force of only 0.46 of an inch of mercury.

#### EXPERIMENT VI.

I also diluted 100 grains of the concentrated acid, in a dish of the same size, with 14 grains of water, and left it, with concentrated acid, under a similar unexhausted receiver standing in mercury, for a period of 23 days, in a stove, the temperature of which (as found by observations made three times a day) ranged from  $76^{\circ}$  to  $96^{\circ}$ , but chiefly between  $85^{\circ}$  and  $91^{\circ}$ ; and though, as



the maximum and minimum temperatures indicate, the evaporating force ranged from 1.03 to nearly 1.9 inch of mercury, the acid allowed to evaporate none of the 14 grains of water with which I had diluted it.

The experiments I have now related, offer conclusive evidence, to those to whom such has hitherto appeared to be wanting, that vapour exists in air as a fluid *sui generis* ; or, that the evaporation of water is not owing to the existence of a chemical affinity between the vapour of that liquid and atmospheric air.

By those convinced that evaporation is not the consequence of a chemical affinity being exerted between vapour and air, two distinct notions have, in the case of evaporation from pure water, been entertained on the reason why evaporation does not go on so rapidly in air as in vacuo : one, that the retardation is owing to the *weight* of the atmosphere ; and the other, that it is owing to the *vis inertie* of the particles of air ; that vapour in ascending from the surface of water into the atmosphere, has to perform a circuitous route, similar to that which water has to take in descending through pebbles ; this reason being consi-



dered to be supported by the circumstance of a vacuum, to which water is exposed, becoming instantaneously saturated with vapour, whilst dry air, on being exposed to water, is a comparatively long time over becoming saturated ; together with the supposed fact, that space, whether full or void of air, is capable of retaining the same quantity of vapour, while the temperature remains the same. However tenable this reason may be as regards evaporation from water, something further seems to claim our adoption in regard to the evaporation of water from diluted sulphuric acid ; for, if the *vis inertię* of the particles of air be the sole cause of the retardation, evaporation, though more slow in air than in vacuo, should go on until *as much water* has left the acid as would leave it in vacuo of the same dryness and at the same temperature,—which does not accord with experiment.

From the results of my experiments, it appears to me unavoidable that we should adopt the notion that the *weight* of the atmosphere is the true cause of the retardation :—it has, however, been asserted, that if the weight was the cause, it would effectually prevent *any* vapour from arising from water below the temperature of  $212^{\circ}$  ; but,



as it is admitted, in support of the argument of the retardation being owing to the *vis inertię* of the particles of air, that the obstruction exerted by the atmosphere to vapour escaping from the surface of water is overcome in proportion to the force of the vapour, and as the force of vapour is increased by an increase of temperature, I see no reason why vapour should not arise from water under atmospheric pressure, at *low* temperatures, and in a degree proportionate to the force of vapour at those temperatures.

I am not aware that other incontrovertible facts have been adduced in support of the notion, that the weight of the atmosphere is the cause of evaporation going on more tardily in air than in vacuo. The fact of water and other liquids boiling, under diminished pressure, at temperatures very low in comparison with the temperatures at which they boil under the usual atmospheric pressure, may, by some, be considered sufficient foundation, whereon to ground such opinion; but, this alone is not indubitable evidence; indeed, it equally supports the opposite notion; for, the characteristic appearance of ebullition being only owing to bubbles of vapour, formed at the bottom of the containing vessel, rushing through the liquid



and bursting forth at its surface,—an effect caused by an equilibrium of force being established in such instance between the tendency of the liquid to assume the elastic state, and the tendency of the atmosphere to resist that change, it certainly would be equally plausible to assert, that this equilibrium takes place at a low temperature, in a vessel exhausted of air, in consequence of the removal of innumerable small particles through which those of vapour must otherwise have filtered, and in order to facilitate this escape past such immovables at the ordinary pressure, the repulsive force of additional heat is indispensable; as it would be to assert, that ebullition takes place, in a vessel exhausted of air, with so little assistance from the repulsive agency of heat, in consequence of the removal of a weight which, in ordinary instances, presses upon the surface of the liquid whose tendency in a free state is to become aeriform.

I cannot but concur in the view held by Dr. Faraday, (Phil. Trans. 1826) that *a limit exists to the production of vapour from bodies*; nor does it appear needful to assign to any other agency than the attraction of cohesion the cause of such limit. And, so far as the experiments



under consideration are concerned, it seems that the weight of the atmosphere, by the slight compression which it exerts, gives some additional cohesion to the particles of liquid; or increases the affinity existing between the acid and the water with which it is diluted, to counterbalance which more of the repulsive agency of heat is required.

Having demonstrated that the evaporation of water from sulphuric acid is capable of being carried further in space void of air, than in space under ordinary atmospheric pressure, it becomes my duty to state the degree of rarefaction of the receivers I have spoken of as exhausted or regarded as *vacua*, and also to state under what degree of pressure the experiments were conducted, which I have described as conducted under unexhausted receivers. As I have for some years regularly registered the indications of the barometer, I am fortunately enabled to furnish with tolerable precision both these requisites. In every instance of an experiment under rarefied air, the exhaustion was such as that the mercury gauge indicated a pressure of only 0.9 of an inch; this being the utmost degree of rarefaction which the state of my pump, during the conducting of



the experiments, would admit of. I will, however, proceed to give the results of the remainder of my experiments, and defer the comparison of pressures to a subsequent part of the paper.

The foregoing experiments were conducted generally at temperatures considerably above the freezing point of water; but, the frost, at the beginning of the year 1838, gave me an opportunity of experimenting at temperatures ranging about that point.

#### EXPERIMENTS VII. AND VIII.

On the 16th January, 1838, 100 grains of sulphuric acid, sp. gr. 1.135, containing 15.8 grains of anhydrous acid, were put into a light evaporating dish of  $2\frac{3}{4}$  inches in diameter. The dish was gently heated upon a sand bath until  $66\frac{1}{2}$  grains of water were expelled; the quantity of acid and water remaining in the dish being only  $33\frac{1}{2}$  grains. The dish with its contents was then placed, along with a vessel containing concentrated acid, under an unexhausted receiver standing in a plate of oil, and left in a place of low temperature.

Into another evaporating dish of the same size,



was also put 100 grains of the acid, sp. gr. 1.135; this was gently heated upon a sand bath, until the 100 grains were reduced to 31.9 grains, by the evaporation of 68.1 grains of water. It was then placed, along with a vessel of concentrated acid, under an exhausted receiver, upon a brass transfer plate, and left in the immediate neighbourhood of the other dish.

The losses of weight from the two dishes were found to be as follows :—

1838.	Total loss from the dish under the unexhausted receiver.	Total loss from the dish under the exhausted receiver.	Range of Temperature to which the objects of experiment were exposed between the present and next previous weighing.
	Grains.	Grains.	
January 19	0.8	6.4	From 28° to 32°
„ 20	0.9	7.0	„ 27 to 30
„ 21	1.0	7.2	„ 27 to 27
„ 22	1.4	8.0	„ 43 to 44
„ 23	1.7	8.1	„ 34 to 37
„ 28	2.6	8.6	„ 30 to 32
„ 31	3.1	8.6	„ 32 to 34
February 3	3.5	8.6	„ 33 to 34
„ 7	4.0		„ 32 to 34
„ 10		8.6	„ 32 to 38

On the 28th January, the acid under the exhausted receiver was in a perfectly crystallized state : after weighing, a little warmth was applied to the dish, by which the acid immediately became fluid, without undergoing any appreciable



change of weight: in this fluid state, it was again left as usual in the place of low temperature, and in a few hours it again became entirely crystallized. In this crystallized state it remained, when the experiment was discontinued, on the 10th of February. It, therefore, appears, that a temperature, ranging from  $30^{\circ}$  to  $32^{\circ}$ , or an evaporating force of from 0.24 to 0.26 of an inch of mercury, was sufficient to concentrate the acid so far as to give it a per centage of 67.8 real or anhydrous acid, and a sp. gr. about 1.7762; and that, while crystallized, it had no apparent further concentration given it by an evaporating force extending even to 0.32 of an inch of mercury.

The acid under the unexhausted receiver continued to lose weight till the 2nd of March; at which time the loss was found to be 6.3 grains: the residue in the dish contained 58.1 per cent. of anhydrous acid, and would have a sp. gr. about 1.6405. The temperature just capable of effecting this degree of concentration was about  $36^{\circ}$ , equal an evaporating force of 0.30 inch of mercury. The atmospheric pressure under which the final concentration was effected, was from 28.34 to 28.97 inches of mercury, as I find on reference to my general register.



I have one other experiment ; but, as it was conducted in a manner similar to the preceding, it may be unnecessary to enter into detail respecting it: it will, perhaps, be enough, if I give its result in the following table, together with the results of those which I have more fully enlarged upon.

Experiments.	Temperature at which the concentration was effected.	Evaporating force by which the concentration was effected.	Pressure under which the concentration was effected.	Degree of concentration effected.	
				Per centage of anhydrous acid.	Specific gravity, at Temp. 60°.
		Inch of Mercury.	Inches of Mercury.		
1st	57°	0.61	0.90	71.53	1.814 *
3rd	48	0.46	0.90	70.69	1.8075
8th	32	0.26	0.90	67.80	1.7762
2nd	17	0.15	29.81	26.78	1.249
4th	48	0.46	29.30	62.77	1.7071
7th	36	0.30	28.34 to 28.97	58.10	1.6405
9th	55	0.58	29.57	66.40	1.7600

From Professor Graham's statements in his

\* The specific gravities here given are from the results of experiments of my own, carefully conducted upon the acid whose degree of purity I have described in a note, page 355, in this paper. And, except in the instance of sp. gr. 1.249, a very remarkable coincidence may be observed to exist, between them and the per centages of anhydrous acid, with those given by Dr. Dalton (*New System of Chemical Philosophy*, vol. 1, part 2, page 404). The per centages given by Dr. Ure in his table (*Chemical Dictionary*) in the same instances appear to be between 2 and 3 too high. The per centage given by Dr. Dalton, in the instance of sp. gr. 1.249, appears to be about 1.8 too low ; and that by Dr. Ure, nearly 1 too high.



paper on "*water as a constituent of salts*," published in the Transactions of the Royal Society of Edinburgh, vol. xiii, part 1, and in the London and Edinburgh Philosophical Magazine, for May, 1835, it would be inferred that a low temperature would not be capable of concentrating sulphuric acid to any considerable strength; for, he therein alludes to having observed a close approximation to the sp. gr. 1.78, in concentrating a dilute acid *at a temperature not exceeding 300°*; and he states that in one experiment, a small quantity of dilute acid was found to concentrate down to three atoms of water to one anhydrous acid (=sp. gr. about 1.66,) *at a temperature not exceeding 212°*. My experiments prove that *so low a temperature as 48°, and exposure to anhydrous air, are enough to concentrate the acid to the sp. gr. 1.7071, if sufficient time be allowed; and a temperature of 55°, to the sp. gr. 1.76.*

The results arranged in the table, will, I believe, be found, at least, near approximations to the truth: and, while they point out to us, in seven individual cases, the particular strengths of acid whose attractions for water counterbalance the evaporating force of anhydrous space, under the several circumstances; they also enable us to form



more correct ideas than we could have done without them, of the strengths of acid required to balance the evaporating force of space under other not widely different atmospheric temperatures and pressures, and afford us some information on the extent to which sulphuric acid is a drier of the atmosphere. Was this the whole amount of the information furnished by them, it would not, I trust, be considered too trifling to support me in the propriety of submitting them to the notice of men of science\*: but, I feel that they more extensively support me, when I find that reflection upon them enables me to furnish information whereby improvement in the more economically conducting the manufacture of sulphuric acid may hereafter most probably be made.

\* Dr. Faraday has remarked (Phil. Magazine, for October, 1833,) that many facts present themselves to observant men, which, though seen by them to be curious, interesting, and new to the world, are not considered worthy of distinct publication: that he has often felt this conclusion to be objectionable; and is convinced that it is better to publish such facts, and even known facts under new forms, provided it be done briefly, clearly, and with no more pretension than the phenomena fairly deserve.



## DR. DALTON'S TABLE,

SHOWING THE EXPANSION OF AIR, AND THE ELASTIC FORCE  
OF AQUEOUS VAPOUR, AT DIFFERENT TEMPERATURES.

Temp.	Volume of air.	Utmost force of aqueous vapour.	Weight of 100 cubic in. of aqueous vapour.	Temp.	Volume of air.	Utmost force of aqueous vapour.	Weight of 100 cubic in. of aqueous vapour.
		in. of Mer	grain.			in. of Mer	grain.
28°	420			53°	501	.54	.354
20	428			54	502	.56	.366
10	438			55	503	.58	.378
0	448	.08		56	504	.59	.384
10	458	.12		57	505	.61	.396
20	468	.17		58	506	.62	.402
30	478	.24		59	507	.64	.414
—	—	—		60	508	.65	.420
32	480	.26	.178	61	509	.67	.432
33	481	.27	.184	62	510	.69	.444
34	482	.28	.191	63	511	.71	.456
35	483	.29	.197	64	512	.73	.468
36	484	.30	.203	65	513	.75	.480
37	485	.31	.209	66	514	.77	.492
38	486	.32	.216	67	515	.80	.509
39	487	.33	.222	68	516	.82	.521
40	488	.34	.229	69	517	.85	.539
41	489	.35	.235	70	518	.87	.551
42	490	.37	.245	71	519	.90	.569
43	491	.38	.255	72	520	.92	.580
44	492	.40	.267	73	521	.95	.598
45	493	.41	.275	74	522	.97	.610
46	494	.43	.284	75	523	1.00	.627
47	495	.44	.293	76	524	1.03	.645
48	496	.46	.303	77	525	1.06	.662
49	497	.47	.313	78	526	1.09	.680
50	498	.49	.323	79	527	1.12	.700
51	499	.50	.329	80	528	1.16	.721
52	500	.52	.341				



I will now advert to the manufacture of sulphuric acid, and make such reviews of the chemical actions which take place in it, as are required to enable me to show in what respect the improvement I have alluded to is to be made.

It is, I think, universally admitted, that dry nitrous acid gas has not the property of changing dry sulphurous acid gas into sulphuric acid; and that it only has that property when water intervenes. The theory of the production of sulphuric acid being, that nitrous acid gas, sulphurous acid gas, and a little water or aqueous vapour meeting together, a mutual action takes place between the three bodies, and a crystalline substance is formed: this crystalline substance is permanent until brought into contact with more water, either in the liquid or vaporous state: when it has had an opportunity of acquiring sufficient water, it is resolved into sulphuric acid and nitrous gas: the latter, immediately taking to itself more oxygen from the atmospheric air in the interior of the chambers, is reconverted into nitrous acid gas; and this, mingling itself with sulphurous acid gas and water, causes a repetition of the operation just mentioned. In this continuous manner the ordinary process of the manufacture of sulphuric acid is conducted.



Now, the only state of the water with which the greater bulk of the mixed gases in the chambers has the opportunity of coming quickly into contact, is the vaporous state ; and when it is considered how little the weight of aqueous vapour is which is capable of existing in a given space, at ordinary atmospheric temperatures, we need not be surprised at the slowness of the process of the manufacture of the acid in question.

At the commencement of the manufacture of the acid, the floors of the chambers are covered either with water or dilute acid ; and therefrom arises, into the aerial space, aqueous vapour, as in other ordinary instances of spontaneous evaporation. Supposing the large quantity of mixed sulphurous and nitrous acid gases to seize with avidity upon the whole of the vapour, and make the aerial space anhydrous ; this anhydrous space would acquire more vapour from the liquid on the floors, and thereby be the means of transferring more water to the newly formed compound, which must be slowly descending, like a fog, towards the liquid on the floors. It is obvious that the greater the amount of vapour existing in the chambers previously to the commencement of the process, and the more quickly the space can be replenished with vapour as the action of the gases



abstracts it, the more quickly must the newly formed compound be enabled to deposit itself in the liquid on the floors ; for, if the compound when newly formed had only a minimum of water, it would be a diffused crystalline body, appearing like a fog ; but if it had an opportunity of speedily acquiring more water, it (the fog-like body) would collect into small drops, and descend, like small rain, with greater speed. And, it is requisite that this compound should get deposited as quickly as possible into the liquid on the floors ; because it is not till it has become thereby diluted, that it emits its supply of nitrous gas for the continuance of the process.

Some manufacturers of sulphuric acid state that they are able to make more acid from a given weight of sulphur, in a given time, in summer than in winter ; but they are not able satisfactorily to account for the difference. I have had the means of fully satisfying myself that such is really the fact ; nor is it, indeed, any other than what strict attention to theory would lead us to anticipate. Let us only consider, that in winter the temperature of the external atmosphere, to which the chambers are exposed, is frequently at  $32^{\circ}$ , and not seldom below that, and that in summer it



often exceeds  $80^{\circ}$ ; and we find that the aerial space of the chambers is capable of receiving from the liquid on the floors four or five times a greater weight of aqueous vapour in summer than in winter, and of transferring it, in a proportionately accelerated rate, to the newly formed combination of gases voracious to receive it. Then, since an abundant supply of aqueous vapour is indispensable to the speedy conversion of sulphurous acid, by nitrous acid, into sulphuric acid, and since the capacity of space for vapour not only increases with an increase of temperature, but even increases in an increasing ratio as the temperature rises, how can it be otherwise than extremely evident that as much sulphur cannot be converted into sulphuric acid, in the same chamber room, and in a given time, in winter as in summer? When the attempt to effect such an object is made, the consequence is, that large portions of the gases pass through the whole range of chambers, and at length escape by the outlet into the external atmosphere, without being condensed; and, indeed, as sulphuric acid chambers are usually managed, a great amount of the gases must in winter be lost in this manner; for, when the temperature of the atmosphere is low, the operator finds a difficulty in keeping the temperature of



the furnace in which the sulphur is burnt, sufficiently high to keep up the combustion, when he attempts to burn only a minimum of sulphur ; and, not having (in many instances) other means of preserving the requisite temperature, he is reluctantly urged to burn more sulphur than circumstances render him capable of converting into, and collecting in the state of, sulphuric acid.

So far, then, I have shown that when the floors of the chambers are covered only with water, or *dilute* acid, there is substantial reason why less sulphuric acid should be collected from a given quantity of sulphur in cold weather than in warm : and, when we take into consideration that the acid on the floors of the chambers is seldom very dilute ; but that it is frequently allowed to be of such strength as to have the sp. gr. 1.45 or 1.50, we find that there is additional reason why cold weather should be objectionable. On reference to the table of the results of my experiments, we see that at the temperature of  $36^{\circ}$ , and at the pressure there stated, the acid was only capable of being concentrated till its per centage was 58.1, =sp. gr. 1.6405, and we may conceive that if the evaporating force of space at the temperature of  $36^{\circ}$ , was just balanced by the attraction of acid



sp. gr. 1.6405, the rate of evaporation from acid sp. gr. 1.45 or 1.50 at the same temperature, must be but very slow, and more especially so at temperatures below  $36^{\circ}$ . Sometimes in severe winter weather the temperature of the chambers is probably as low as  $17^{\circ}$ ; and my experiments show that when the temperature is only  $17^{\circ}$ , and the pressure about 29.8 inches of mercury, the acid can only be concentrated so far as to have the per centage 26.78, = sp. gr. about 1.249; the fact, therefore, is, that in a case of so low a temperature as  $17^{\circ}$ , no evaporation whatever could take place from the acid, if its sp. gr. was greater than 1.249; and, consequently, in such a case, the process of the manufacture of sulphuric acid must be entirely stopped, was it not that aqueous vapour was supplied from some other source. Indeed, *some* vapour always is supplied otherwise than from the acid on the floors: some enters the chambers with the air by which the combustion is supported; but, when the temperature of that air is so low as  $17^{\circ}$ , or  $20^{\circ}$ , or  $30^{\circ}$ , the weight of the vapour admitted along with it is too trifling to be of much avail in an instance of so great a demand. It has for some time been a practice among some manufacturers of the acid, to turn steam, issuing from a pipe connected with a vessel of boiling



water, into the chambers\* : this must have a particularly beneficial effect, when the temperature of the chambers would otherwise have been as low as I have just alluded to, but it has also disadvantages : its beneficial effect cannot last much longer than during the time the steam is allowed to enter the chambers ; and it is imprudent to allow it to do so long, because the great cooling power of the chambers causes the steam to condense nearly as quickly as it enters ; and by continuing to admit it, the acid on the floors would soon become much diluted ; the consequence of which would be, that the manufacturer would have

\* Though steam is sometimes thus used, it is not because those who use it have a correct knowledge of the great importance of the continual generation and existence of steam (in the scientific acceptation of the term, invisible vapour) in the chambers. They use it, from the understanding that it—steam of  $212^{\circ}$ , or thereabout—must necessarily be condensed on entering the cold chambers ; and in the resulting water falling as rain or fog, the gases readily meet with the water dispersed for their action—the condensed steam, therefore, carrying the sulphuric acid down along with it ;—nor do they seem to be aware of the fact, that if the temperature of the interior of the chambers was so high as to hold (supposing the absence of acid and the gases) in an uncondensed and invisible state the steam admitted, that even then the gases would, if admitted, supply themselves from that steam with the requisite water, and that strong liquid acid would fall, though the temperature might be great enough to retain pure water in the state of invisible steam.



to be at much additional expense in concentrating it when removed from the chambers.

Having explained my views to a friend, he, during the last winter, and when his chambers were not working well in consequence of the severe cold, had a vessel of water so placed in the furnace as that the hot gases were enabled to convey along with them into the chambers a comparatively large quantity of vapour : and this plan cannot but have been attended with some benefit ; yet, the benefit must have been highly inadequate, because, as in the case of steam turned in from a pipe, the vapour thus admitted would be speedily condensed by the cold chambers.

It is quite evident that the great desideratum is to be enabled to give the whole interior of the chambers, at all times, a temperature not less than that of summer ; nor do I think that a doubt can reasonably be entertained that a temperature considerably higher than the maximum temperature of summer would be attended with a corresponding beneficial effect. Consequently, what I suggest as an improvement in the working of sulphuric acid chambers, is that leaden pipes should be caused so to pass through the interior of the chambers as that when the steam of boiling water



is allowed to pass through them they will communicate warmth, or even hotness (if the same should upon trial be found to give additional benefit), to the whole internal aerial space of the chambers: and, it does not seem to be of much consequence whether the pipes be laid through the acid on the floors, or only through the space immediately above that liquid;\* for, in either case, the aerial space would become heated. Such a contrivance would be of benefit in two ways;—it would heat and supply the aerial space with vapour, and would, inevitably, at the same time, be considerably concentrating, instead of diluting, the liquid acid on the floors.†

It may be said, that in the foregoing remarks I have not taken into consideration that the heat, conveyed into the chambers from the furnace

\* Perhaps the greatest advantage would be obtained if the pipes were laid both through the liquid and through the space above the liquid.

† It is advisable, that in erecting chambers attention should be given to their form: those having the least cooling surface, in relation to their internal capacity, being the most preferable. If the form of a cube be departed from, it should be in the depth: indeed, from what I have said (page 383) regarding the necessity of the quickly depositing of the crystalline substance, it may be inferred that there is chemical reason why they should be less deep than cubical, independently of the fact that in such case they will more firmly support themselves.



where the sulphur is burning, must prevent the interior of the chambers from ever having so low a temperature as the external atmosphere in winter : to which I must reply, that towards the extremity of a range of several chambers there will not, I think, be found *much* difference between the internal and the external temperature : but, even admitting that a considerable difference exists between the internal and the external temperature throughout the whole range, let the argument be extended to summer temperature as well as to winter, and the result will give greater support to my views ; for, then, for the same reason, it must be allowed that the internal temperature must be much higher than the external temperature, in the shade, ( $80^{\circ}$  for instance, as before mentioned) ; and to this I may add that as the chambers are generally exposed to the direct heating influence of the solar rays, the internal temperature must, from that direct action of solar heat alone, be very much higher than the temperature in the shade without. And, as the capacity of space for vapour increases in an *increasing* ratio as the temperature rises, the very much greater speed with which the aerial space is supplied with vapour in summer than in winter is undeniable.

Bolton-le-Moors, May 28th, 1838.



## APPENDIX

## TO THE FOREGOING PAPER.

I perceive, under the head Sulphuric Acid, in the last of the monthly parts of Dr. Ure's "*Dictionary of Arts, Manufactures, and Mines*," which is just turned out from the press, that an experiment has been made by M. Clement-Desormes, expressly to ascertain the effect of an elevated temperature in causing the process of the formation of sulphuric acid to go on freely; the result of which showed the beneficial application of the temperature of  $100^{\circ}$ , in promoting the active agency of the aqueous vapour upon the gases. It is highly gratifying to find that my anticipations, arrived at from theoretical reasoning, are in such a satisfactory manner corroborated by direct experiment.

From the conclusion of this experiment of M. Clement-Desormes, Dr. Ure seems to recommend maintaining the temperature of sulphuric acid chambers at  $100^{\circ}$ :—this he would do by the admission of a jet of steam; it being discharged



from a high pressure boiler loaded with forty pounds upon the square inch. He says that it serves, by powerful agitation, not only to mix the different gaseous molecules intimately together, but to impel them against each other, and thus bring them within the sphere of their mutual chemical attraction. The mechanical commotion which must be produced, by the sudden freedom from confinement of a body having the elastic force of steam under a pressure of forty pounds upon the square inch, would, I admit, be advantageous if sufficient agitation of the gaseous molecules was not derivable from another source: but, when we consider the comparatively enormous bulk of the aeriform bodies which has to be condensed into one cubic inch in the formation of a cubic inch of sulphuric acid, or of the crystalline compound produced from sulphurous acid, nitrous acid, and a minimum of water, surely our imagination will not allow us to suppose that the agitation which takes place, in tending to restore the equilibrium disturbed by such condensation, is not sufficient to intermix and diffuse amongst each other the several kinds of gaseous molecules, leaving out of consideration the general law of the diffusion of aeriform bodies experimentally illustrated by Dr. Dalton, in the Manchester Memoirs,



Vol. 1, second series : and, from the very active manner in which combination of the gases is known to take place when plenty of aqueous vapour is present, I cannot conceive that any additional impulse is required. Dr. Ure admits that the chemical agency of steam is more important than its mechanical agency ; and, in this I fully agree with him : but, of course, for the reason given in my foregoing paper, I do not concur with him in thinking it advisable that the steam should be furnished by a jet from a boiler, but that it is preferable for it to be derived from the liquid on the floors of the chambers. Not admitting the necessity of its mechanical agency, high pressure steam is essentially no more beneficial than low pressure steam ; because, from the conversion of it to the liquid state, it is not capable of communicating to the interior of the chambers any higher a temperature than low pressure steam, since the same *weight* of steam, whether under high or low pressure, contains exactly the same quantity of caloric.

H. H. WATSON.

Bolton, April 1st, 1839.





Watson, Henry Hough. 1842. "On the Relative Attractions of Sulphuric Acid for Water under Particular Circumstances; with Suggestion of Means of Improving the Ordinary Process of Manufacturing Sulphuric Acid." *Memoirs of the Literary and Philosophical Society of Manchester* 6, 352–393.

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