

January 15, 1844.—The President in the Chair.

The following presents were announced since the last Meeting :—

“Lessons on Chemistry,” by W. H. Balmain, from the author.

“Two Lectures on the application of Physiology in Rearing and Feeding Cattle,” by Lyon Playfair, Ph.D., from the author.

Douglas MacLagan, M.D., and G. E. Day, M.D., were elected Members of the Society; and Mr. John Thom an Associate.

The following communications were then read :—

XCV. *Experiments on the Heat disengaged in Combinations.*

By THOMAS GRAHAM, Esq., F.R.S., &c. (*Was resumed.*)

Part II. *Neutralization of various Acids by Hydrate of Potash.*

THE arrangements adopted for observing the heat evolved on neutralizing acids by potash were similar to those described in the former paper. The same platinum crucible, weighing 1201·9 grains, and hollow cylinder of palladium, weighing 207·6 grains, were employed as the containing vessel and stirrer; but the constant quantity of water employed as a vehicle for the acid and alkali was increased from 1000 grains to 1544 grains, or 100 grammes, while the equivalent quantities of the substances used were the same as before. The solution of the saline body formed in an experiment was consequently one-half more dilute, and the small but sensible

52 Mr. Graham on the Heat disengaged in Combinations.

effect of further dilution of the solution in producing cold, observable in some of the former experiments, was thus entirely avoided, while the increase of the mass of fluid reduced the influence of external causes on its temperature. A mercurial thermometer of greater delicacy was employed, of which the bulb was a cylinder of 1.25 inch in length and 0.3 inch in diameter; the scale was graduated into degrees Fahrenheit, ranging from 40° to 70° , each degree being 0.42 inch in length (0.74 inch for one degree centigrade), divided into tenths of a degree, each of which could again be subdivided into fifths by the eye, so that the observation was made to one-fiftieth of a degree Fahrenheit. The eye was directed to the scale through a straight cylindrical tube of small diameter, supported in a horizontal position. The mercury in the bulb of the thermometer was equivalent in capacity for heat to 11.5 grains of water, and the containing vessel and stirrer to 49 grains, making together 60.5 grains of water; the capacity of the salt dissolved or formed rarely exceeded that of 12 grains of water.

I. *Neutralization of Hydrate of Potash by Nitric and Hydrochloric Acids.*

The equivalent proportion of this acid adopted in these experiments is 33.85 grains, that is one-twentieth of 677, the usual equivalent of nitric acid on the oxygen scale. Nearly one-half the quantity mentioned was used in an experiment, namely 0.455 equivalent, diluted in the crucible with about four-fifths of the water, while the remaining portion of the 1544 grains of water, in a small and thin glass flask, contained hydrate of potash in quantity sufficient to saturate the acid, and leave a *slight* excess of alkali. The two liquids were afterwards brought to exactly the same temperature, which was observed by two thermometers, the corresponding points of which were accurately determined, and the potash solution then emptied into the nitric acid. The following are the results of three observations of the temperature of the liquids before mixture, and the temperature after mixture:—

Before mixture . . .	61°·91	62°·13	62°·13
After mixture . . .	66°·70	66°·91	66°·89
Rise of temperature .	4°·79	4°·78	4°·76

Increasing $4^{\circ}78$ the mean of the experiments, in the proportion of 0.455 to 1, we have $10^{\circ}50$ as the rise of temperature on saturating a whole equivalent of potash by nitric acid.

The heat evolved upon combination is sensibly affected by a considerable difference in the temperatures at which the acid and alkali are mixed; being less at the lower temperature.

Mr. Graham on the Heat disengaged in Combinations. 53

This appears by the following experiments, in which 0·5 equivalent of nitric acid was neutralized at a temperature twenty-two degrees lower than in the former experiments.

Before mixture . . .	40°·25	40°·60	
After mixture . . .	45°·43	45°·80	
Rise of temperature .	5°·18	5°·20	Mean 5°·19.

Hence we have the heat from the neutralization of nitric acid by hydrate of potash—

10°·50, at 62° F.
10°·38, at 40° F.

Half an equivalent of hydrochloric acid, 11·38 grains, was neutralized with hydrate of potash in slight excess, exactly as the nitric acid was treated in the preceding experiment.

Before mixture . . .	60°·20	60°·00	59°·95
After mixture . . .	65°·30	65°·15	65°·10
Rise of temperature .	5°·10	5°·15	5°·15

Mean rise 5°·13 for 0·5 equivalent of hydrochloric acid, or 10°·26 for 1 equivalent of that acid. The neutralization of hydrate of potash, therefore, in very dilute solutions with these two different acids produces nearly the same disengagement of heat, the result with nitric acid being 10°·50.

The heat of combination appears also to be sensibly affected in amount by the temperature of the experiment:—

Before mixture . . .	40°·00	40°·25	
After mixture . . .	45°·02	45°·30	
Rise of temperature .	5°·02	5°·05	Mean 5°·03

From which it follows that the heat from the neutralization of hydrochloric acid by hydrate of potash is—

10°·26, at 60° F.
10°·06, at 40° F.

It is remarkable how large a proportion the cold produced on dissolving in water crystallized nitrate of potash and chloride of potassium, the salts produced in these experiments, bears to the heat observed in the formation of the same salts.

One equivalent of crystallized nitrate of potash (63·25 grs.) well dried, pounded and sifted, was dissolved in the usual quantity of water:—

Before solution . . .	61°·80	62°·20	61°·88
After solution . . .	56°·10	56°·45	56°·18
Fall of temperature	5°·70	5°·75	5°·70 Mean 5°·72.
Before solution . . .	56°·45	57°·70	55°·45
After solution . . .	50°·80	52°·00	49°·75
Fall of temperature	5°·65	5°·70	5°·70 Mean 5°·68.

54 Mr. Graham on the Heat disengaged in Combinations.

The cold on dissolving this salt is not quite constant, but increases sensibly at low temperatures, a law which appears to prevail in a class of salts:—

Before solution .	47°·00	46°·40	45°·95
After solution .	41°·05	40°·47	40°·00
Fall of temperature	$\frac{5^{\circ}95}{5^{\circ}95}$	$\frac{5^{\circ}93}{5^{\circ}93}$	$\frac{5^{\circ}95}{5^{\circ}95}$ Mean 5°·94.

It appears, on comparing the last set of experiments with that immediately preceding it, that a difference of ten degrees at this part of the scale makes a difference of 0°·26, or 1·22nd part, in the fall of temperature consequent upon the solution of an equivalent of nitrate of potash. It is this increased absorption of heat at the low temperature probably which occasions the observed heat of combination of the salt to diminish at the same part of the scale.

On the other hand, the cold, on dissolving several equivalents of nitrate of potash successively at a constant temperature, in the same quantity of water diminishes considerably with the number of equivalents of salt dissolved. The capacity for heat of the crystallized salt is 0·239 (Regnault).

Dissolved in 1544 grains of water,

First equivalent of nitrate of potash:—

	62°·34	63°·68
	56°·68	57°·90
Fall	$\frac{5^{\circ}66}{5^{\circ}66}$	$\frac{5^{\circ}78}{5^{\circ}78}$ Mean 5°·72.

Second equivalent of nitrate of potash:—

	63°·47	63°·12
	58°·17	57°·86
Fall	$\frac{5^{\circ}30}{5^{\circ}30}$	$\frac{5^{\circ}26}{5^{\circ}26}$ Mean 5°·28.

Third equivalent of nitrate of potash:—

	63°·40	63°·56
	58°·47	58°·61
Fall	$\frac{4^{\circ}93}{4^{\circ}93}$	$\frac{4^{\circ}95}{4^{\circ}95}$ Mean 4°·94.

Fourth equivalent of nitrate of potash:—

	63°·57	63°·35
	58°·95	58°·76
Fall	$\frac{4^{\circ}62}{4^{\circ}62}$	$\frac{4^{\circ}59}{4^{\circ}59}$

Fifth equivalent of nitrate of potash:—

	63°·40	63°·34
	59°·08	59°·10
Fall	$\frac{4^{\circ}32}{4^{\circ}32}$	$\frac{4^{\circ}24}{4^{\circ}24}$ Mean 4°·28.

Sixth equivalent of nitrate of potash:—

	63°·45
	69°·63
Fall	$\frac{3^{\circ}82}{3^{\circ}82}$

Mr. Graham on the Heat disengaged in Combinations. 55

In consequence of this diminished absorption of heat in the solution of the latter equivalents of nitrate of potash, the addition of water to the strong solution finally obtained occasions a further absorption of heat; or dilution produces cold.

The last prepared solution, which consisted of 379·5 grains of nitrate of potash dissolved in 1544 grains of water, and is a solution nearly saturated for the temperature, was mixed with another 1544 grains of water in a pint silver crucible with silver spatula, weighing 1650 grains, both liquids being at the same temperature:—

Before mixture . . .	63°·19
After mixture . . .	61°·91
Fall of temperature . .	<u>1°·28</u>

A second portion of 1544 grains of water being added to the above solution, occasioned a further fall of temperature:—

Before mixture . . .	63°·57
After mixture . . .	63°·19
Fall	<u>0°·38</u>

It appears from these experiments on the solution of successive equivalents of nitrate of potash in the same quantity of water, that much of the cold on dissolving that salt is properly referable to the dilution of the solution, and not to the simple liquefaction or solution of the crystalline salt. But this is more obvious in dissolving a salt of great solubility, such as nitrate of ammonia, of which many more equivalents may be dissolved in succession.

Dissolved in 1544 grains of water,
100·4 grains, or 2 equivalents of nitrate of ammonia:—

66°·25
57°·91
Fall <u>8°·34</u>

Third and fourth equivalents:—

66°·43
58°·91
Fall <u>7°·52</u>

Fifth and sixth equivalents:—

66°·21
59°·36
Fall <u>6°·85</u>

Seventh and eighth equivalents:—

66°·10
59°·82
Fall <u>6°·28</u>

Ninth and tenth equivalents:—

66°·26
60°·41
Fall <u>5°·85</u>

56 Mr. Graham on the Heat disengaged in Combinations.

Eleventh and twelfth equivalents:—

66°·53

61°·06

Fall $\overline{5^{\circ}47}$

Thirteenth and fourteenth equivalents:—

66°·45

61°·29

Fall $\overline{5^{\circ}16}$

Fifteenth and sixteenth equivalents:—

66°·47

61°·55

Fall $\overline{4^{\circ}92}$

Seventeenth and eighteenth equivalents:—

66°·61

61°·99

Fall $\overline{4^{\circ}62}$

Nineteenth and twentieth equivalents:—

66°·26

61°·91

Fall $\overline{4^{\circ}35}$

Twenty-first and twenty-second equivalents:—

66°·58

62°·45

Fall $\overline{4^{\circ}13}$

Twenty-third and twenty-fourth equivalents:—

66°·66

62°·63

Fall $\overline{4^{\circ}03}$

Twenty-fifth and twenty-sixth equivalents:—

66°·83

63°·16

Fall $\overline{3^{\circ}67}$

Twenty-seventh and twenty-eighth equivalents:—

66°·53

62°·97

Fall $\overline{3^{\circ}56}$

Twenty-ninth and thirtieth equivalents:—

66°·57

63°·24

Fall $\overline{3^{\circ}33}$

Thirty-first and thirty-second equivalents:—

66°·80

63°·57

Fall $\overline{3^{\circ}23}$

Thirty-third and thirty-fourth equivalents:—

66°·37

63°·24

Fall $\overline{3^{\circ}13}$

Thirty-fifth and thirty-sixth equivalents:—

66°·45

63°·50

Fall $\overline{2^{\circ}95}$

Here we find that while the fall on the solution of the first two equivalents of nitrate of ammonia is $8^{\circ}34$, that of the last two dissolved is only $2^{\circ}95$, or little more than a third of the former. The liquid, however, finally consisted of 1544 grains of water and 1807·2 grains of salt, and would therefore have a considerably greater capacity for heat than the water alone; but the proper correction for this increase of capacity cannot at present be made, as the specific heat of nitrate of ammonia has not been ascertained.

Mr. Graham on the Heat disengaged in Combinations. 57

The last solution of nitrate of ammonia, which was nearly saturated for the temperature, was of density $1^{\circ}247$. Three portions of 100 grammes of water were added to it in succession, to discover the cold produced on dilution.

First 100 grammes of water :—

Before mixture . . .	$66^{\circ}83$
After mixture . . .	$60^{\circ}27$
Fall	$6^{\circ}56$

Second 100 grammes of water :—

Before mixture . . .	$67^{\circ}06$
After mixture . . .	$64^{\circ}40$
Fall	$2^{\circ}66$

Third 100 grammes of water :—

Before mixture . . .	$67^{\circ}06$
After mixture . . .	$65^{\circ}61$
Fall	$1^{\circ}45$

The high solubility of the nitrate of soda adapts it for similar experiments. It will be observed that a difference of 13 degrees of temperature does not materially affect the amount of heat absorbed on dissolving a single equivalent of this salt. The capacity for heat of the crystallized salt is 0.278 (Regnault).

One equivalent of nitrate of soda, 53.40 grains, dissolved in 100 grammes of water :—

Before solution . . .	$65^{\circ}07$	$51^{\circ}78$	$51^{\circ}63$
After solution . . .	$61^{\circ}56$	$48^{\circ}25$	$48^{\circ}08$
Fall	$3^{\circ}51$	$3^{\circ}53$	$3^{\circ}55$

Ten equivalents of this salt being dissolved successively in the same 100 grammes of water, the following changes of temperature were observed :—

	I.	II.	III.	IV.	V.
	$65^{\circ}07$	$65^{\circ}01$	$64^{\circ}63$	$64^{\circ}80$	$64^{\circ}84$
	$61^{\circ}56$	$61^{\circ}70$	$61^{\circ}65$	$63^{\circ}14$	$62^{\circ}29$
Fall .	$3^{\circ}51$	$3^{\circ}31$	$2^{\circ}98$	$2^{\circ}66$	$2^{\circ}55$
	VI.	VII.	VIII.	IX.	X.
	$64^{\circ}77$	$64^{\circ}63$	$64^{\circ}89$	$64^{\circ}77$	$64^{\circ}64$
	$62^{\circ}38$	$62^{\circ}34$	$62^{\circ}74$	$62^{\circ}79$	$62^{\circ}76$
Fall .	$2^{\circ}39$	$2^{\circ}29$	$2^{\circ}15$	$1^{\circ}98$	$1^{\circ}88$

The solution of the tenth equivalent of this salt produces therefore only one-half the cold due to the first equivalent.

The solution of chloride of potassium in water is attended with a fall of temperature, which is considerable, although not so great as with nitrate of potash.

58 Mr. Graham on the Heat disengaged in Combinations.

One equivalent of chloride of potassium (46·62 grains) dissolved in 100 grammes of water :—

Before solution . . .	62°·05	61°·80	61°·70	
After solution . . .	59°·10	58°·88	58°·75	
Fall of temperature . .	<u>2°·95</u>	<u>2°·92</u>	<u>2°·95</u>	Mean 2°·94.

At a lower temperature :—

Before solution . . .	45°·55	45°·04	45°·53	
After solution . . .	42°·55	42°·02	42°·50	
Fall of temperature . .	<u>3°·00</u>	<u>3°·02</u>	<u>3°·03</u>	Mean 3°·02.

II. Neutralization of Hydrate of Potash by Sulphuric Acid.

Half an equivalent of sulphuric acid, 12·53 grains, was saturated with a slight excess of hydrate of potash, the united liquids containing 100 grammes of water, as in the preceding experiments with nitric and hydrochloric acids :—

Before mixture . . .	61°·31	61°·45	61°·53	
After mixture . . .	67°·01	67°·13	67°·21	
Rise	<u>5°·70</u>	<u>5°·68</u>	<u>5°·68</u>	Mean 5°·69.

The rise of temperature on saturating a whole equivalent of hydrate of potash with sulphuric acid will therefore be 11°·38.

The saturation of sulphate of water, already in combination with sulphate of potash in the bisulphate of that base, is attended with the disengagement of a still greater quantity of heat. Half an equivalent of fused bisulphate of potash, dissolved in water like the acid of the former experiments, was neutralized by potash, with the usual conditions :—

Before mixture . . .	62°·74	62°·92	63°·05	
After mixture . . .	68°·95	69°·12	69°·22	
Rise	<u>6°·21</u>	<u>6°·20</u>	<u>6°·17</u>	Mean 6°·19.

The saturation of the whole equivalent of sulphate of water in a solution of the bisulphate of potash therefore occasions the disengagement of 12°·38; free sulphate of water only 11°·38; the excess in the former case being 1°·00.

Now, in saturating two equivalents of sulphuric acid, the heat evolved is twice 11°·38, or 22°·76; but as 12°·38 is evolved in saturating the second equivalent of sulphuric acid, it follows that 10°·38 only are evolved in saturating the first equivalent of acid. Hence we have—

Heat disengaged in the formation of bisulphate of potash	10°·38	
... .. saturating acid of	...	12°·38
		<u>22°·76</u>

The cold, on dissolving an equivalent of crystallized sul-

Mr. Graham on the Heat disengaged in Combinations. 59

phate of potash, 54·55 grains, in 100 grammes of water, was also observed :—

Before solution . . .	66°·69	66°·01	66°·27	
After solution . . .	64°·38	63°·75	63°·96	
Fall	<u>2°·31</u>	<u>2°·26</u>	<u>2°·31</u>	Mean 2°·29.

On mixing solutions of sulphate of potash and sulphate of water (dilute sulphuric acid), to form bisulphate of potash, cold is produced, as was formerly observed; and from this cause sulphate of potash, when dissolved in water acidulated with sulphuric acid, produces more cold than in pure water, by about one-third of the quantity from the latter. This excess of heat absorbed I was disposed to connect with the combination of sulphate of water with sulphate of potash, and formation of a double salt. But it is remarkable that the magnesian sulphates, which we do not certainly know to combine with hydrated acids, as sulphate of potash does, likewise produce greater cold on dissolving in acidulated than in pure water.

Thus an equivalent of crystallized sulphate of magnesia, which dissolves in 1000 grains of water with a fall of 0°·88 R. (Chemical Memoirs, vol. i. p. 111), dissolved in the same quantity of water already containing an equivalent of sulphuric acid with a fall of 1°·12, 1°·17, 1°·18 R. in three experiments; of which the mean is 1°·16, being 0°·28 more than in pure water. A second equivalent of crystallized sulphate of magnesia, when dissolved in the same liquor, produced a fall, in three experiments, of 0°·96, 0°·92, 0°·95 R., of which the mean is 0°·94, or only 0°·06 more than in pure water.

In an equivalent of nitric or of hydrochloric acid, the fall from the solution of an equivalent of crystallized sulphate of magnesia was nearly double what it is in pure water.

The fall in water containing 1 equivalent of nitric acid was 1°·70, 1°·68, 1°·64, of which the mean is 1°·67.

The fall in water containing 1 equivalent of hydrochloric acid was 1°·70, 1°·70, 1°·68; mean 1°·69 R.

The fall on the solution of 1 equivalent of sulphate of magnesia in $\frac{1}{2}$ equivalent of hydrochloric acid was 1°·37, 1°·37, 1°·38; mean 1°·37 R. The excess of cold produced by the half equivalent of this acid, over water alone, was therefore 0°·50; the excess by the whole equivalent of acid 0°·82; so that fully more than one-half of the effect is produced by the first half equivalent of acid.

An excess above 1 equivalent of acid to 1 equivalent of a salt of this class increases the depression of temperature still further, but in a less degree than the direct proportion of its

60 Mr. Graham on the Heat disengaged in Combinations.

quantity. Thus the cold on dissolving 1 equivalent of sulphate of zinc in water being $1^{\circ}\cdot02$ R.,—

In $1\frac{1}{4}$ equivalent of sulphuric acid, $1^{\circ}\cdot22$, $1^{\circ}\cdot19$, $1^{\circ}\cdot25$; mean $1^{\circ}\cdot22$.

In 1 equivalent of nitric acid, $1^{\circ}\cdot56$, $1^{\circ}\cdot55$, $1^{\circ}\cdot54$; mean $1^{\circ}\cdot55$.

In $\frac{1}{2}$ equivalent of hydrochloric acid, $1^{\circ}\cdot50$, $1^{\circ}\cdot50$, $1^{\circ}\cdot47$; mean $1^{\circ}\cdot49$.

In 1 equivalent of hydrochloric acid, $1^{\circ}\cdot82$, $1^{\circ}\cdot83$, $1^{\circ}\cdot86$; mean $1^{\circ}\cdot83$.

In 2 equivalents of hydrochloric acid, $2^{\circ}\cdot26$, $2^{\circ}\cdot26$, $2^{\circ}\cdot24$; mean $2^{\circ}\cdot25$.

The solution of an equivalent of crystallized sulphate of iron was attended with a fall of temperature,—

In water of $1^{\circ}\cdot06$ R.

In 1 equivalent of sulphuric acid, of $1^{\circ}\cdot28$, $1^{\circ}\cdot20$, $1^{\circ}\cdot26$, $1^{\circ}\cdot25$; mean $1^{\circ}\cdot25$.

In 1 equivalent of hydrochloric acid, of $1^{\circ}\cdot69$, $1^{\circ}\cdot68$, $1^{\circ}\cdot73$; mean $1^{\circ}\cdot70$.

The solution of an equivalent of crystallized sulphate of copper was attended with a fall of temperature,—

In water of $0^{\circ}\cdot63$ R.

In 1 equivalent of sulphuric acid, of $0^{\circ}\cdot94$, $0^{\circ}\cdot96$, $1^{\circ}\cdot02$; mean $0^{\circ}\cdot97$ R.

The mixture of an equivalent of *sulphate of water*, 30·68 grains, in 300 grains of water, with another 700 grains of water, occasioned a rise of $0^{\circ}\cdot09$ R.; with 700 grains of water containing 1 equivalent of hydrochloric acid a rise of $0^{\circ}\cdot16$, and with 700 grains of water containing 1 equivalent of nitric acid, $0^{\circ}\cdot00$.

The magnesian sulphates generally resemble sulphate of water in producing heat and not cold on dilution of their strong solutions. The solutions of the three following salts were saturated in the cold :—

Sulphate of zinc (density 1·395), with equal bulk of water, $+0^{\circ}\cdot60$.

Sulphate of magnesia (density 1·294), with equal bulk of water, $+0^{\circ}\cdot60$.

Protosulphate of iron (density 1·227), with equal bulk of water, $+0^{\circ}\cdot04$.

The experiments on the solution of salts in acids leave it doubtful, whether the additional depression of temperature is due in every case and entirely to a combination of the salt with the acid, as it may be supposed to be when sulphate of potash is dissolved in dilute sulphuric acid, bisulphate of potash being then formed, or whether it is a consequence of a

Mr. Graham on the Heat disengaged in Combinations. 61

partial decomposition of the salt by the free acid to which it is exposed. The small portion of acid, generally a single equivalent, which produces the greatest proportional effect, seems to indicate that combination or decomposition is the cause, rather than any alteration in the solvent power of the liquid. The action of hydrochloric acid and of nitric acid is often the same, and is greater than that of sulphuric acid. This appears even in the solution of a magnesian chloride in water and in these acids.

Thus 42.29 grains, 1 equivalent, of the fused anhydrous chloride of zinc were dissolved in 1000 grains of water with a rise in two experiments of $3^{\circ}42$, $3^{\circ}45$ R., of which the mean is $3^{\circ}44$ R. In 1000 grains of water containing 1 equivalent of sulphuric acid, with a rise of $3^{\circ}43$, $3^{\circ}42$, $3^{\circ}42$ R., in three experiments; which is nearly the same result as in pure water. In the same quantity of water containing 1 equivalent of hydrochloric acid, with a rise of $2^{\circ}86$, $2^{\circ}88$, $2^{\circ}86$; of which the mean is $2^{\circ}87$ R., being $0^{\circ}57$ less heat than in water alone. The presence of the hydrochloric acid has therefore occasioned a fall of $0^{\circ}57$ in the solution of chloride of zinc, while the action of sulphuric acid is insensible.

An alkaline chloride was little affected by the presence of an equivalent of these acids in the water in which it was dissolved. Thus *chloride of sodium* was dissolved with a fall—

In 1000 grs. water,	of $0^{\circ}57$, $0^{\circ}60$,	Mean $0^{\circ}59$ R.
... .. + HCl,	of $0^{\circ}60$, $0^{\circ}60$, $0^{\circ}60$,	... $0^{\circ}60$ R.
... .. + NO ₃ ,	of $0^{\circ}50$, $0^{\circ}50$, $0^{\circ}52$,	... $0^{\circ}51$ R.
... .. + SO ₃ ,	of $0^{\circ}50$, $0^{\circ}50$, $0^{\circ}43$,	... $0^{\circ}48$ R.

To obtain light upon this influence of acids on the thermal phenomena of the solution of salts, experiments were made upon two other salts. *Sulphate of ammonia* without any water of crystallization (1 equivalent, or 41.41 grains) was observed to dissolve in 1000 grains of water with a fall of $0^{\circ}51$ R. In water containing $\frac{1}{2}$ HCl, with a fall of $1^{\circ}12$, $1^{\circ}10$, and $1^{\circ}12$ R.; mean $1^{\circ}11$. In water containing HCl, with a fall of $1^{\circ}30$, $1^{\circ}22$, $1^{\circ}28$; mean $1^{\circ}27$ R. In water containing NO₃, with a fall of $1^{\circ}28$, $1^{\circ}30$, $1^{\circ}30$; mean $1^{\circ}29$ R. In water containing SO₃, with a fall of $0^{\circ}92$, $0^{\circ}92$, $0^{\circ}90$; mean $0^{\circ}92$ R. The addition of a second equivalent of highly diluted sulphuric acid to the last solution produced a change of temperature in three experiments of $0^{\circ}02$, $0^{\circ}00$, $0^{\circ}00$. The addition of a second equivalent of sulphate of ammonia to the preceding solutions of the bisulphate of ammonia, occasioned a fall of $0^{\circ}58$, $0^{\circ}55$, $0^{\circ}60$ R.; mean $0^{\circ}58$, or very little more than in pure water

62 Mr. Graham *on the Heat disengaged in Combinations.*

(0°·51). In 1544 grains of water containing 1 equivalent of acetic acid (32·15 grains), with a fall of 0°·84, 0°·78, 0°·81 F., of which the mean is 0°·81 F., the experiment being made at 67° F. In 1 equivalent of oxalic acid (22·64 grains), with a fall of 1°·20, 1°·21 and 1°·22 F., the experiment being made at 65° F. To render the last two experiments comparable with the former, they must be reduced in the proportion of 19 to 13, that is, the effect of the acetic acid to 0°·55 R., of the oxalic acid to 0°·83 R.; so that the influence of the acetic acid is almost nothing, of the oxalic acid much less than that of the mineral acids.

While 1 equivalent of *nitrate of potash* was dissolved in 1000 grains of water at 63° F., with a fall of 3°·76, 3°·72 and 3°·80 R., of which the mean is 3°·76; it was dissolved in the same quantity of water containing 1 equivalent of nitric acid at 67° F., with a fall of 3°·64, 3°·54, 3°·64 R., of which the mean is 3°·57; in the same quantity of water containing 1 equivalent of sulphuric acid at 58° F., with a fall of 3°·53, 3°·50, 3°·50 R., of which the mean is 3°·51.

The mere mixing of solutions of such neutral salts as are understood to combine together and form a double salt, is not attended with such changes of temperature. No sensible change of temperature was perceived on mixing dilute solutions of a magnesian and potash sulphate; and one of these salts was dissolved in a solution of the other with the same fall of temperature as in pure water. Although I think it all but certain that these salts combine at once on mixing, I could not discover a single circumstance which was decisive of the fact. The density of such a mixture of salts was not altered by boiling it alone or with spongy platinum, and was exactly the same as that of the liquid formed on dissolving in water a corresponding quantity of the crystallized double sulphate. The addition of an equivalent of sulphuric acid already highly diluted to each of the solutions thus compared, produced exactly the same fall of temperature. On the other hand, this fall of temperature was as nearly as possible the same as that obtained on dividing the acid into two equal portions, and mixing separately a solution of each of the constituent salts with each portion. The solution of a double salt appears therefore to be as nearly as possible equivalent to the constituent salts dissolved apart. Even in the formation of *alum* no certain change of temperature was observable; one-fourth of an equivalent of sulphate of potash (13·63 grains), when dissolved in 1000 grains of water, producing a fall of 0°·32 R., while when dissolved in 1000 grains of water containing one-fourth of $\text{Al}_2\text{O}_3 + 3\text{SO}_3$, the fall was 0°·35, 0°·32, 0°·35 R.,

Mr. Graham on the Heat disengaged in Combinations. 63

of which the mean is $0^{\circ}34$; the experiments being made at 57° F.

But these double sulphates being all less soluble than their constituent sulphates, it was desirable to make the experiment upon the formation of a double salt, which is more soluble than its constituents; such as the double chloride of mercury and ammonium. One-half of an equivalent of chloride of mercury, 42.70 grains, was dissolved in 1544 grains of water at 64° F., with a fall of $0^{\circ}29$, $0^{\circ}30$, $0^{\circ}30$ F., of which the mean is $0^{\circ}30$ F. The same quantity of chloride of mercury was dissolved in 1544 grains of water, containing half an equivalent, 16.74 grains, of chloride of ammonium, at 63° F., with a fall of $0^{\circ}13$, $0^{\circ}12$, $0^{\circ}12$ F., of which the mean is $0^{\circ}12$ F. Doubling these results, we have the fall from a whole equivalent of chloride of mercury in water equal to $0^{\circ}60$; from chloride of mercury in chloride of ammonium $0^{\circ}24$; the difference, or $0^{\circ}36$, being due to heat evolved in the formation of the double salt. The latter, however, or sal-alembroth, assumes an atom of water of crystallization in its formation, which may perhaps occasion some change of temperature.

When 1 equivalent of chloride of mercury was dissolved in half an equivalent of chloride of ammonium at 63° , the fall was $0^{\circ}45$, $0^{\circ}45$, $0^{\circ}47$ F., of which the mean is $0^{\circ}46$ F. The disengagement of heat in the formation of this second double salt is therefore $0^{\circ}60 - 0^{\circ}46 = 0^{\circ}14$ F. It is doubtful whether the heat here can be ascribed to hydration; as the resulting double salt has been crystallized at the usual temperature by Dr. Kane, both anhydrous and with one atom of water. The circumstance however of the chloride of mercury being dissolved by a solution of sal-ammoniac in much larger quantity than by pure water, affords a proof of the immediate formation of a double salt on the solution of its constituents together, which cannot be obtained in the magnesian or aluminous double sulphates.

I may be allowed to place under the present head of sulphuric acid, the results of experiments on the solution in water of two double sulphates, namely sulphate of zinc and soda, and sulphate of manganese and soda, no experiment on a double salt of the soda division of this class being recorded in the former paper. The *sulphate of zinc and soda*, formed by Mr. Arrott, was in excellent crystals, containing four atoms of water; of which the composition is expressed by the formula $\text{ZnO}, \text{SO}_3 + \text{NaO}, \text{SO}_3 + 4 \text{HO}$. One-half of an equivalent, 58.61 grains of the salt, containing 11.25 grains of water of crystallization, was dissolved in 988.8 grains of water

64 Mr. Graham on the Heat disengaged in Combinations.

at 62° F., with a fall in three experiments of 0°·02 R., 0°·04, 0°·02; mean 0°·03 R.

Of the same salt made anhydrous by heat and fused, half an equivalent, or 47·41 grains, was dissolved in 1000 grains of water at 62° F., with a rise in three experiments of 1°·86, 1°·87, 1°·84; mean 1°·86 R. Doubling the results of the experiments in both cases, to obtain the changes for a whole equivalent, we find—

Cold on solution of $\text{ZnO}, \text{SO}_3 + \text{NaO}, \text{SO}_3 + 4 \text{HO}$ 0°·06 R.
Heat on solution of $\text{ZnO}, \text{SO}_3 + \text{NaO}, \text{SO}_3$ 5°·72 R.

As the two sulphates, in all the double sulphates of this class containing sulphate of soda, crystallize apart when the salt is dissolved in water at 62°, the double salt is probably decomposed in these experiments; and the circumstances of its solution may therefore be very different from those of a magnesian double sulphate containing sulphate of potash.

The *sulphate of manganese and soda*, for which I am also indebted to Mr Arrott, was in good crystals containing two atoms of water; the formula of this salt being $\text{MnO}, \text{SO}_3 + \text{NaO}, \text{SO}_3 + 2 \text{HO}$. 1 equivalent of the crystallized salt, 103·2 grains, containing 11·25 grains of water of crystallization, was dissolved in 988·8 grains of water, with a rise of temperature in three experiments of 0°·77, 0°·70, and 0°·70; of which the mean is 0°·72 R.

Of the same salt, fused by heat and anhydrous, 1 equivalent, 91·95 grains, was dissolved in 1000 grains of water, with a rise in two experiments of 3°·02 and 2°·99; of which the mean is 3°·00 R. The results, therefore, for this double salt, are—

Heat on solution of $\text{MnO}, \text{SO}_3 + 2 \text{HO}$. . . 0°·72
... .. MnO, SO_3 3°·00

III. Neutralization of Bichromate of Potash by Hydrate of Potash.

Half an equivalent of bichromate of potash, 47·34 grains, and a little more than half an equivalent of hydrate of potash contained separately in different portions of the usual quantity 1544 grains or 100 grammes of water, were brought to the same temperatures exactly, and mixed in two experiments:—

Before mixture . . .	63°·23	63°·50
After mixture . . .	67°·71	67°·97
Rise of temperature .	4°·48	4°·47

Doubling 4°·48, the mean result, we have 8°·96 F. as the heat evolved on neutralizing the second equivalent of chromic acid in bichromate of potash.

Mr. Graham on the Heat disengaged in Combinations. 65

Of the neutral or yellow chromate of potash, which is the product of this neutralization, 1 equivalent, 62·08 grains, was dissolved by 1544 grains of water at 65° F., with a fall in three experiments of 1°·82, 1°·81 and 1°·87, of which the mean is 1°·83.

IV. *Neutralization of Acetic Acid by Hydrate of Potash.*

Half an equivalent of acetic acid, 16·08 grains, was neutralized by potash in very slight excess, as in the other experiments:—

Before mixture . . .	63°·52	63°·81	63°·94
After mixture . . .	68°·68	68°·98	69°·12
Rise of temperature .	5°·16	5°·17	5°·18

The mean result of these experiments 5°·17 being doubled, we have 10°·34 F. as the heat evolved on the saturation of acetic acid by hydrate of potash.

Of acetate of potash fused without becoming black, 1 equivalent, 61·65 grains, was dissolved in 1544 grains of water at 65° F., with a rise of temperature in three experiments of 2°·45, 2°·47, 2°·44; of which the mean is 2°·45 F.

V. *Neutralization of Oxalic Acid by Hydrate of Potash.*

Half an equivalent of oxalic acid was neutralized by potash under the usual circumstances:—

Before mixture . . .	64°·60	64°·66	64°·69
After mixture . . .	69°·84	69°·89	69°·95
Rise of temperature .	5°·24	5°·23	5°·26

Doubling 5°·24, the mean result, we have 10°·48 F. as the heat evolved on the saturation of a whole equivalent of oxalic acid by hydrate of potash.

One equivalent of *crystallized oxalic acid*, 39·50 grains, containing 12·5 grains of water of crystallization, was dissolved in 1533 grains of water at 67° F., with a fall of 3°·04, 3°·06, 3°·04; of which the mean is 3°·05.

One equivalent of *oxalate of water* deprived of its water of crystallization, 28·25 grains, was dissolved in 1544 grains of water at 67° F., with a fall of 0°·99, 0°·99, 1°·01; of which 1°·00 is the mean. The difference between the falls on solution of the hydrated and anhydrous oxalate, is occasioned by the hydration of the latter on solution. The heat disengaged when oxalate of water combines with its two atoms of constitutional water is therefore 3°·05—1°·00=2°·05 F.

Neutral *oxalate of potash* crystallizes with a single atom of water, which requires a heat of 212° to expel it. 1 equi-

66 Mr. Graham on the Heat disengaged in Combinations.

valent of the crystallized salt, 57·76 grains, containing 6·25 grains of water, was dissolved in 1538 grains of water at 67° F., with a fall of 2°·65, 2°·66 and 2°·67; of which the mean is 2°·66 F.

Of the same salt made anhydrous by heat, one-half of an equivalent, 25·75 grains, was dissolved in 1544 grains of water, with a fall of 0°·76, 0°·71, 0°·74; of which the mean is 0°·74. A whole equivalent of the salt would therefore have dissolved with a fall of 1°·58, which is 1°·08 less than the fall from the hydrated salt. The last quantity represents the heat of combination of oxalate of potash with one atom of water of crystallization. It approaches nearly to one-half of the heat disengaged by oxalate of water, in combining with two atoms of water, one-half of 2°·05 being 1°·025; the difference is within the errors of observation.

When hydrated oxalate of potash is dissolved in water containing oxalic acid, the change of temperature is very much the same as in pure water, although in the former case a superoxalate will be formed. One-fourth of an equivalent of oxalate of potash, 14°·44 grains, was dissolved in 1544 grains of water containing in solution one-fourth of an equivalent of hydrated oxalic acid, at 67° F., with a fall of 0°·70, 0°·68, 0°·68; mean 0°·68 F. If it were therefore possible to dissolve a whole equivalent of the salt in a whole equivalent of the acid contained in the quantity of water to which we are restricted, the fall would be four times greater, or 2°·72 F., which is nearly the same as the cold on dissolving crystallized oxalate of potash in water, namely 2°·66. Here again little or no heat is observed in forming a double salt, for the binoxalate of potash must be regarded as such.

Binoxalate of Potash. $\text{KO}, \text{C}_2\text{O}_3 + \text{HO}, \text{C}_2\text{O}_3, 2 \text{HO}$.—As with bisulphate of potash, the saturation of the excess of acid in this salt causes the disengagement of more heat than the saturation of the same quantity of free acid. One-fourth of an equivalent of the crystallized binoxalate, 22·91 grains, was neutralized by hydrate of potash at 67°:—

Before mixture . . .	66°·80	66°·85	66°·96	
After mixture . . .	69°·91	69°·96	70°·04	
Rise of temperature .	3°·11	3°·11	3°·08	Mean 3°·10

The mean quantity, multiplied by four, gives 12°·40 F., as the heat evolved on neutralizing by potash the second equivalent of oxalic acid in binoxalate of potash. Now distributing the heat from the saturation of two equivalents of oxalic acid, 20°·68 ($= 10°·34 \times 2$), as was done in sulphuric acid, we have—

Mr. Graham on the Heat disengaged in Combinations. 67

Heat disengaged in the formation of binoxalate of pot.	8°28
... .. in saturating acid of binoxalate of pot.	12°40
	<u>20°68</u>

One-fourth of an equivalent of binoxalate of potash, 22·91 grains, containing 6·25 grains of water of crystallization, was dissolved in 1538 grains of water at 64° F., with a fall of 1°·65, 1°·66, 1°·65; mean 1°·65 F. The mean result multiplied by four, gives 6°·60 F. as the fall on dissolving a whole equivalent of binoxalate of potash in water. This is 0°·89 more than the sum of the falls on dissolving the constituent salts separately, 2°·66 + 3°·05 being equal to 5°·71 only.

Quadroxalate of Potash. $\text{KO}, \text{C}_2\text{O}_3 + \text{HO}, \text{C}_2\text{O}_3 + 2(\text{HO}, \text{C}_2\text{O}_3 + 2\text{HO})$.—Four-sixths of an equivalent of hydrated oxalic acid, 26·22 grains, were mixed with one-sixth of an equivalent of potash exactly to form this salt:—

Before mixture . . .	64°25	64°23	64°25
After mixture . . .	66°01	66°01	65°99
Rise of temperature .	<u>1°76</u>	<u>1°78</u>	<u>1°74</u>

The mean result 1°·76 multiplied by six, gives 10°·56 as the heat evolved in the formation of quadroxalate of potash; that is, in the saturation of 1 equivalent of potash by 1 of oxalic acid, and the further combination of that oxalate of potash with 3 equivalents of oxalate of water. This rise of temperature is nearly the same as that in the formation of neutral oxalate of potash, namely 10°·48.

To observe the heat disengaged on neutralizing quadroxalate of potash by hydrate of potash, one-sixth of an equivalent of that acid salt in solution was mixed with three-sixths of an equivalent, or rather more, of the alkali, so as to form neutral oxalate:—

Before mixture . . .	64°19	64°20	64°51
After mixture . . .	69°38	69°42	69°71
Rise of temperature .	<u>5°19</u>	<u>5°22</u>	<u>5°20</u>

Doubling 5°·20, the mean result, we have 10°·40 F. as the heat disengaged on saturating 1 equivalent of potash by each of the 3 atoms of oxalate of water in the quadroxalate of potash.

0·192 equivalent (30·70 grains) of quadroxalate of potash was dissolved in 1540 grains of water at 63°, with a fall of 2°·02, 2°·13, 2°·14; of which the mean is 2°·10 F. This gives by calculation a fall of 10°·93 for the solution of a whole equivalent of quadroxalate of potash, which is 0°·88 less than the fall of its constituent salts dissolved separately, 2°·66 with three times 3°·05 amounting to 11°·81.

68 Mr. Graham on the Heat disengaged in Combinations.

The different oxalates enumerated appear to absorb quantities of heat, on dissolving, which have a simple relation to each other. Thus, dividing the different falls of temperature by $0^{\circ}\cdot88$, a number which has more than once presented itself in the discussion of these experiments, we obtain a set of ratios given in the second column; and which, being multiplied by two in the third column, approach nearly to round numbers:—

	I. Cold on solution.	II. Ratios.	III. Ratios.	
Cr. oxalate of potash . . .	$2^{\circ}\cdot66$	$3^{\circ}\cdot02$	$6^{\circ}\cdot04$	6.
Cr. oxalic acid	$3^{\circ}\cdot05$	$3^{\circ}\cdot47$	$6^{\circ}\cdot94$	7.
Cr. binoxalate of potash .	$6^{\circ}\cdot60$	$7^{\circ}\cdot50$	$15^{\circ}\cdot00$	15.
Cr. quadroxalate of potash	$10^{\circ}\cdot93$	$12^{\circ}\cdot42$	$24^{\circ}\cdot84$	25.

VI. Neutralization of Bicarbonate of Potash with Hydrate of Potash.

Half an equivalent of the crystallized salt, $31\cdot38$ grains, dissolved in water, was neutralized with hydrate of potash:—

Before mixture . . .	$67^{\circ}\cdot28$	$67^{\circ}\cdot93$	$67^{\circ}\cdot68$
After mixture . . .	$70^{\circ}\cdot66$	$71^{\circ}\cdot24$	$71^{\circ}\cdot03$
Rise of temperature .	$3^{\circ}\cdot38$	$3^{\circ}\cdot31$	$3^{\circ}\cdot35$

Doubling $3^{\circ}\cdot35$, the mean result, there is obtained $6^{\circ}\cdot70$ as the heat disengaged on saturating the second proportion of carbonic acid in the bicarbonate of potash.

One equivalent, $62\cdot76$ grains, of the crystallized bicarbonate was dissolved in 100 grammes of water at 67° , with a fall in three experiments of $3^{\circ}\cdot68$, $3^{\circ}\cdot69$ and $3^{\circ}\cdot74$; mean $3^{\circ}\cdot70$.

One equivalent of anhydrous carbonate of potash was dissolved in 100 grammes of water at 67° , with a rise in three experiments of $2^{\circ}\cdot48$, $2^{\circ}\cdot43$ and $2^{\circ}\cdot47$; mean $2^{\circ}\cdot46$. The heat evolved on dissolving anhydrous acetate of potash is nearly the same, being $2^{\circ}\cdot45$.

VII. Neutralization of Arsenic and Phosphoric Acids by Hydrate of Potash.

Half an equivalent of arsenic acid, $36\cdot00$ grains, in solution as usual, was mixed with exactly half an equivalent of hydrate of potash, to form the binarsenate of potash ($2\text{HO}, \text{KO}, \text{AsO}_5$):—

Before mixture . . .	$63^{\circ}\cdot04$	$63^{\circ}\cdot19$	$63^{\circ}\cdot29$
After mixture . . .	$68^{\circ}\cdot14$	$68^{\circ}\cdot30$	$68^{\circ}\cdot38$
Rise of temperature .	$5^{\circ}\cdot10$	$5^{\circ}\cdot11$	$5^{\circ}\cdot09$

Doubling $5^{\circ}\cdot10$, the mean result, we obtain $10^{\circ}\cdot20$ F. as

Mr. Graham on the Heat disengaged in Combinations. 69

the heat disengaged by neutralizing 1 equivalent of potash in the formation of binarsenate of potash.

One-fourth of an equivalent of arsenic acid, 18·00 grains, was mixed with exactly half an equivalent of potash, to form arseniate of potash ($\text{HO}, 2\text{KO}, \text{AsO}_5$):—

Before mixture . . .	63°·27	63°·33	63°·42
After mixture . . .	67°·87	67°·94	68°·05
Rise of temperature .	4°·60	4°·61	4°·63 Mean 4°·61.

Twice 4°·61, or 9°·22 F., is therefore the heat disengaged on neutralizing 1 equivalent of hydrate of potash in the formation of the neutral arseniate of potash.

The same salt was formed by mixing together solutions of half an equivalent of binarsenate of potash, 56·37 grains, and exactly half an equivalent of potash:—

Before mixture . . .	64°·28	64°·27	64°·20
After mixture . . .	68°·31	68°·33	68°·26
Rise of temperature .	4°·03	4°·06	4°·06

Taking 4°·05 as the mean, we have twice that quantity, or 8°·10 F., as the heat disengaged on neutralizing 1 equivalent of potash with the acid in binarsenate of potash.

On forming the subarsenate of potash ($3\text{KO}, \text{AsO}_5$), by mixing together solutions of one-sixth of an equivalent of arsenic acid and exactly half an equivalent of potash:—

Before mixture . . .	63°·41	63°·50	63°·50
After mixture . . .	67°·40	67°·52	67°·49
Rise of temperature .	4°·09	4°·02	3°·99

Doubling 4°·03, the mean result, we have 8°·06 F. as the heat disengaged in the formation of one-third of an equivalent of subarsenate of potash, or in the neutralization of each of 3 equivalents of potash by a single equivalent of arsenic acid.

Hence the successive addition of 3 equivalents of potash to 1 of arsenic occasions the following disengagements of heat:—

By first KO 10°·20; formation of binarsenate of potash.
 ... second KO 8°·10; formation of arseniate of potash.
 ... third KO 5°·88; formation of subarsenate of potash.
 $24°·18 = 8°·06 \times 3$.

Of hydrated phosphoric acid, which had been boiled in water for a considerable time to render it fully tribasic, half an equivalent was mixed with half an equivalent of potash, to form biphosphate of potash ($2\text{HO}, \text{KO}, \text{PO}_5$):—

Before mixture . . .	64°·00	64°·00	64°·03
After mixture . . .	69°·01	68°·99	69°·02
Rise of temperature .	5°·01	4°·99	4°·99

70 Mr. Graham on the Heat disengaged in Combinations.

Taking $5^{\circ}00$ as the mean, we have $10^{\circ}00$ F. as the heat disengaged on saturating 1 equivalent of potash with 1 equivalent of phosphoric acid in the formation of biphosphate of potash, containing $KO + 2HO$ as bases.

By mixing one-fourth of an equivalent of phosphoric acid with half an equivalent of potash, phosphate of potash ($HO, 2KO, PO_5$) was formed :—

Before mixture . . .	$64^{\circ}00$	$63^{\circ}61$	$63^{\circ}63$
After mixture . . .	$68^{\circ}49$	$68^{\circ}08$	$68^{\circ}18$
Rise of temperature .	$4^{\circ}49$	$4^{\circ}47$	$4^{\circ}55$

Doubling the mean result, $4^{\circ}50$, we have $9^{\circ}00$ F. as the heat disengaged in forming half an equivalent of neutral phosphate of potash, or in saturating each of 2 equivalents of potash by 1 equivalent of phosphoric acid, in the formation of phosphate of potash.

The same phosphate of potash was formed by mixing solutions of half an equivalent of biphosphate of potash with half an equivalent of potash :—

Before mixture . . .	$64^{\circ}06$	$64^{\circ}14$	$64^{\circ}15$
After mixture . . .	$68^{\circ}09$	$68^{\circ}15$	$68^{\circ}16$
Rise of temperature .	$4^{\circ}03$	$4^{\circ}01$	$4^{\circ}01$

Doubling $4^{\circ}02$, the mean result, we have $8^{\circ}04$ F. as the heat disengaged on saturating an equivalent of potash with the acid of biphosphate of potash.

To form the subphosphate of potash ($3KO, PO_5$), one-sixth of an equivalent of phosphoric acid, 7.43 grains, was mixed with half an equivalent of potash :—

Before mixture . . .	$63^{\circ}61$	$63^{\circ}67$	$63^{\circ}69$
After mixture . . .	$67^{\circ}87$	$67^{\circ}93$	$67^{\circ}99$
Rise of temperature .	$4^{\circ}26$	$4^{\circ}26$	$4^{\circ}30$

Twice the mean result, $4^{\circ}27$, is $8^{\circ}54$ F., which is the heat disengaged on neutralizing each of 3 equivalents of potash by a single equivalent of phosphoric acid.

The heat therefore disengaged in the gradual saturation of phosphoric acid by 3 equivalents of potash may be thus distributed :—

By first	equivalent of potash	. .	$10^{\circ}00$	
... second	$8^{\circ}08$	
... third	$7^{\circ}54$	
				$25^{\circ}62 = 8.54 \times 3.$