ART. XII.—*The Heat of Formation of Trisodium Orthophosphate, Trisodium Orthoarsenate, the Oxides of Antimony, Bismuth Trioxide; and fourth paper on the Heat of Combination of Acidic Oxides with Sodium Oxide;* by W. G. MIXTER.

[Contributions from the Sheffield Chemical Laboratory of Yale University.]

THE heat of combination of an acidic oxide with sodium oxide may be derived from the heat of formation of the anhydrous salt, and, conversely, the thermal effect of the union of the elements in a salt may be calculated from the heat of combination of the oxides forming it. Only the latter method is applicable to insoluble salts of weak acids, as, for example, sodium antimonate. The investigation includes new determinations of some constants and the results obtained agree with those of other investigators and show the value of the sodium-peroxide method.

Kilogram-calories, which are indicated by the decimal point, are used in some of the calculations for sake of brevity. The gram-calorie is, however, more philosophical, as the gram is the unit of mass in physical science and quantities in chemistry are commonly expressed in grams. Unless otherwise indicated, the constants used in the calculations are Thomsen's and are taken from his Thermochemistry, the English translation by Katharine A. Burk.

Trisodium Orthophosphate.

The red phosphorus for the work was digested with hot dilute nitric acid, next with a concentrated solution of sodium hydroxide and then washed and dried. When exposed to moist air for twenty-four hours, it gained in weight 0·16 per cent. The following are the experimental data:

	1	2
Phosphorus	1·000 gram	1·000 gram
Sodium peroxide	12 "	13 "
Water equivalent of system	4,136 "	3,999 "
Temperature interval	1·986°	2·004°
Heat observed	8,214^c	8,014^c
" of oxidation of iron	−48^c	−48^c
For 1 gram of phosphorus	8,166^c	7,966^c

In the first experiment the mixture was in a silver cup the rim of which only was in contact with the cold sides of the bomb. With this arrangement the fusion cools slowly and

the reaction is more complete than without the inner cup, as was the case in the second experiment. Using the first result we have

$5Na_2O_2 + 2P\,(8166 \times 62) = 3Na_2O,P_2O_5 + 2Na_2O +$ 506,292^c
$5Na_2O + 5O = 5Na_2O_2 +$ ..... 97,000^c*
$3Na_2O + 2P + 5O = 3Na_2O,P_2O_5 +$ ..... 603,292^c
$2P + 5O = P_2O_5 +$ ..... 369,900^c
$3Na_2O + P_2O_5 = 3Na_2O, P_2O_5 +$ ..... 233,392^c

In the Physikalisch-Chemischen Tabellen with reference to Berthelot† $3Na,P,4O = 452{\cdot}4^c$, from which is derived $235{\cdot}5^c$ for the heat effect of $Na_2O+P_2O_5$. Berthelot‡ and Thomsen both found the heat of neutralization of phosphoric acid by sodium hydroxide to be 34·0. From this we derive $Na,P,O_4,Aq = 469{\cdot}5^c$. Joly§ gives the following: $Na_3PO_8\,24HO = -14{\cdot}5^c$ and $Na_3PO_8+24HO = +48{\cdot}1^c$. (O = 8.) The heat of solution of Na_3PO_4 is the sum of these numbers, i. e., $33{\cdot}6^c$. The experimental data are not given and the writer does not understand the result, which is apparently twice too high. Subtracting one-half of it, $16{\cdot}8^c$, from $469{\cdot}5^c$ we have $Na_3,P,O_4 = 452{\cdot}7^c$, which is essentially the same as given in the Physikalisch-Chemischen Tabellen, as stated above.

From the result of experiment 1 we have

$3Na_2O + 2P + 5O = 2Na_3PO_4 +$ ..... $603{\cdot}3^c$
$6Na + 3O = 3Na_2O + (99{\cdot}8 \times 3) +$ ..... $299{\cdot}4^c$
$2(3Na + P + 4O) =$ ..... $902{\cdot}7^c$
$3Na + P + 4O =$ ..... $451{\cdot}4^c$

The heat of formation of sodium phosphate found by the two methods is $452{\cdot}7^c$ and $451{\cdot}4^c$, and hence the heat of combination of sodium oxide with phosphorus pentoxide obtained by the different methods is, essentially, the same.

Trisodium Orthoarsenate.

The arsenic for the following experiments was sublimed and then heated in a current of dry hydrogen in order to remove any oxide present.

	1	2	3
Arsenic	5·000 gr.	5·000 gr.	6·000 gr.
Sodium peroxide	23 "	19 "	22 "
Water equivalent of system	4,028 "	3,945 "	3,994 "
Temperature interval	2·667°	2·865°	3·247°

* De Forcrand, C. R., cxxvii, 514.
† Ann. Ch. Phys. (5), ix, 28.
‡ Loc. cit. § C. R., civ, 1704.

Heat observed	10,743^c	11,309^c	12,969^c
" of oxidation of iron	−48^c	−48^c	−48^c
" " oxygen absorbed	−58^c	−90^c	−67^c
	10,637^c	11,171^c	12,854^c
For 1 gram of arsenic	2,127^c	2,234^c	2,132^c

The mean of the results is 2,168^c and for 150 grams of arsenic it is 325·2^c. The heat of combination of sodium oxide with arsenic pentoxide is derived thus:

$5Na_2O_2 + 2As = 3Na_2O, As_2O_5 + 2Na_2O +$	325·2
$5Na_2O + 5O = 5Na_2O_2 +$	97·0
$3Na_2O + 2As + 5O = 3Na_2O, As_2O_5 +$	422·2
$2As + 5O = As_2O_5$	219·4
$3Na_2O + As_2O_5 = 3Na_2O, As_2O_5 +$	202·8

Two determinations of the heat of union of arsenic pentoxide with sodium oxide gave for 1 gram of the former 792^c and 867^c respectively. The combustions were not satisfactory, as a little sodium arsenite was formed. Using the higher result, we have $867 \times 230 = 194{,}400^c$ for the heat effect of $3Na_2O + As_2O_5$.

The heat of formation of trisodium orthoarsenate is derived as follows:

$3Na_2O + 2As + 5O = 2Na_3AsO_4 +$	422·2
$3Na_2 + 3O = 3Na_2O +$	299·4
$2Na_3, As, O_4 =$	721·6^c
$Na_3, As, O_4 =$	360·8^c

The heat of formation of trisodium arsenate in solution calculated from Thomsen's heat of neutralization of arsenic acid is 381·3; subtracting 17·7, the heat of solution of Na_3AsO_4 (Joly),* gives 363·6 for Na_3,As,O_4.

Antimony.

A mixture of pulverized antimony and sodium peroxide does not burn throughout the mass when kindled at one point, hence sulphur or some other substance must be added to the mixture to furnish the heat required to effect the combustion. The following are the experiments:

	1	2
Antimony	10·000 grams	10·000 grams
Sulphur	1·000 "	1·000
Sodium peroxide	31 "	30 "
Water equivalent of system	4,028 "	4,222
Temperature interval	4·384°	4·208°

* C. R., civ, 1704.

Heat observed	17,660^c	17,766^c
" of oxidation of sulphur	−5,271^c	−5,271^c
" " " " iron	−48^c	−48^c
" " oxygen absorbed	−60^c	−72^c
	12,281^c	12,375^c

The mean result for 240·4 grams of antimony is 296,300^c. As an excess of sodium oxide was present in the fusions Na_3SbO_4 must have been formed, hence we have

$5Na_2O_2 + 2Sb + 2Na_3SbO_4 + 2Na_2O +$	296,300^c
$5Na_2O + 5O =$	97,000^c
$3Na_2O + 2Sb + 5O = 2Na_3SbO_4 +$	393,300^c

Antimony Pentoxide.

The preparation of the pentoxide was made as follows: antimony was completely oxidized by prolonged digestion with hot concentrated nitric acid, and the antimonic acid obtained was washed to remove soluble impurities. It was converted into oxide by heating in an electric furnace until the weight remained constant at about 400°. The product was allowed to cool in a closed tube, as antimony pentoxide absorbs water from the air. It was free from a lower oxide and 1·7662 grams yielded 1·6784 grams of Sb_2O_4, which is equivalent to 1·7662 grams of Sb_2O_5. For the following experiments antimony pentoxide was weighed in a stoppered bottle and mixed with the sulphur and sodium peroxide in a closed bomb.

	3	4	5
Antimony pentoxide	10·059 gr.	10·007 gr.	10·673 gr.
Sulphur	2·000 "	2·000 "	2·000 "
Sodium peroxide	21 "	23 "	21 "
Water equivalent of system	4,100 "	4,028 "	4,034 "
Temperature interval	3·789°	3·834°	3·900°
Heat observed	15,535^c	15,444^c	15,733^c
" of oxidation of sulphur	−10,542^c	−10,542^c	−10,542^c
" " " " iron	−48^c	−48^c	−48^c
" " oxygen evolved	+151^c		+359^c
	5,096^c	4,854^c	5,502^c
For 1 gram of Sb_2O_5	507^c	485^c	515^c

The result of 4 should not be included in the final value as the oxygen evolved was lost. The mean of the other two is 511 and for 320·4 grams it is 163,700^c.

Antimony Trioxide.

Antimony trioxide was made by treating the trichloride with dilute ammonia, washing the product thoroughly and then

heating it out of contact with air as long as water came off. It was free from a higher oxide.

The experimental data are as follows:

	6	7	8
Antimony trioxide	9·985 gr.	10·318 gr.	8·994 gr.
Sulphur	2·000 "	1·800 "	2·200 "
Sodium peroxide	28 "	25 "	28 "
Water equivalent of system	4,110 "	4,097 "	4,182 "
Temperature interval	4·190°	4·008°	4·209°
Heat observed	17,221c	16,417c	17,602c
" of oxidation of sulphur	−10,542c	−9,488c	−11,596c
" " " " iron	−48c	−48c	−48c
	6,631c	6,881c	5,958c
For 1 gram	664c	667c	662c

The oxygen absorbed or evolved in each of the combustions was insignificant. Different mixtures were taken in order to learn whether or not the thermal result is influenced by the proportions of antimony trioxide, sulphur and sodium peroxide. The fact that the results are the same indicates that the same sodium antimonate was formed in each instance.

The mean of the experiments is 664 and for one gram molecule of antimony trioxide it is 191,500c.

Antimony Tetroxide.

Antimony tetroxide was made by heating antimonic acid in an electric furnace until the product did not lose weight at a dull red heat. In the following experiments the absorption of oxygen was insignificant:

	9	10
Antimony tetroxide	10·233 grams	7·386 grams
Sulphur	2·000 "	2·000 "
Sodium peroxide	23 "	22 "
Water equivalent of system	4,161 "	4,180 "
Temperature interval	3·871°	3·486°
Heat observed	16,107c	14,571c
" of oxidation of sulphur	−10,542c	−10,542c
" " " " iron	−48c	−48c
	5,517c	3,981c
For 1 gram	539c	539c

The result for 304·4 grams of antimony tetroxide is 164,100c.

In all of the combustions of antimony and its oxides the oxidation was complete and no antimonite was formed. The

solutions of the fusions were tested adding silver nitrate and then ammonia. No black substance remained, proving that an antimonite was not present. The insoluble residues from the fusions when treated with a boiling solution of potassium hydroxide, silver nitrate and ammonia also yielded no black substance. The insoluble residues mentioned even after long digestion with water reacted alkaline, showing that the hydrolysis of the sodium antimonate was not complete.

The heat of formation of the oxides of antimony is derived from the experimental results as follows:

$3Na_2O + 2Sb + 5O = 2Na_3SbO_4 +$	393·3
$3Na_2O + Sb_2O_5 = 2Na_3SbO_4 +$	163·7
$2Sb + 5O = Sb_2O_5 +$	**229·6**
$2Na_2O_2 + Na_2O + Sb_2O_3 = 2Na_3SbO_4 +$	191·5
$2Na_2O + 2O = 2Na_2O_2 +$	38·8
$3Na_2O + Sb_2O_3 + 2O = 2Na_3SbO_4 +$	230·3
$3Na_2O + Sb_2O_5 = 2Na_3SbO_4 +$	163·7
$Sb_2O_3 + 2O = Sb_2O_5 +$	**66·6**
$Na_2O_2 + 2Na_2O + Sb_2O_4 = 2Na_3SbO_4 +$	164·1
$Na_2O + O = Na_2O_2 +$	19·4
$3Na_2O + Sb_2O_4 + O = 2Na_3SbO_4 +$	183·5
$3Na_2O + Sb_2O_5 = 2Na_3SbO_4 +$	163·7
$Sb_2O_4 + O = Sb_2O_5 +$	**19·8**
$2Sb + 5O = Sb_2O_5 +$	229·6
$Sb_2O_4 + O = Sb_2O_5 +$	19·8
$2Sb + 4O = Sb_2O_4 +$	**209·8**
$2Sb + 5O = Sb_2O_5 +$	229·
$Sb_2O_3 + 2O = Sb_2O_5 +$	66·
$2Sb + 3O = Sb_2O_3 +$	**163·0**

Thomsen derived the heat of formation of antimonic acid from that of the pentachloride and the heat effect of the hydrolysis of it and obtained $Sb_2, O_5, 3H_2O = 228{\cdot}8^c$, the writer found that $Sb_2, O_5 = 229{\cdot}6^c$. The difference between these two numbers is within the limits of error. Thomsen stated that the antimonic acid was free from chlorine and the writer has also found that the hydrolysis of antimony pentachloride is complete. Evidently the heat effect $Sb_2O_5, 3H_2O$ is quite

small, as might be expected, since As_2O_5, $3H_2O$=6·5^c only, while P_2O_5, $3H_2O$ = 30·6^c.

In conclusion it may be stated that the heat of formation of trisodium antimonate from its elements is 346·4^c, and is derived as follows:

$3Na_2O + 2Sb + 5O = 2Na_3SbO_4 +$ ..... 393·3^c
$6Na + 3O = 3Na_2O +$ ..... 299·4^c
$6Na + 2Sb + 8O = 2Na_3SbO_4 +$ ..... 692·7^c
$3Na + 2Sb + 4O = Na_3SbO_4 +$ ..... 346·4^c

Bismuth Trioxide.

Pulverized bismuth was burned in experiment 1. The trioxide was made by heating pure basic bismuth nitrate in a combustion tube to dull redness until acid fumes ceased to come off. A weighed portion of the oxide was found not to lose weight after fusion. The following are the experiments:

	1		3
Bismuth	20·000 gr.		
" unburned	0·995 "		
" burned	19·005 "		
" trioxide		20·000 gr.	20·000 gr.
Sulphur	1·000 "	2·000 "	2·000 "
Water equivalent of system	3,935 "	4,256 "	4,005 "
Temperature interval	3·347°	3·445°	3·642°
Heat observed	13,170^c	14,662^c	14,586^c
" of oxidation of sulphur	−5,271^c	−10,542^c	−10,542^c
" " " " iron	−48^c	−48^c	−48^c
" " oxygen set free	−60^c	−28^c	−48^c
	7,791^c	4,044^c	3,948^c
For 1 gram	410^c	202^c	197^c

In calculating the heat of formation of bismuth trioxide it makes no difference what sodium salt is formed in the fusion since the same one results from the action of sodium peroxide on both metallic bismuth and its trioxide. Moreover, assuming that a different peroxide is formed than Bi_2O_5 does not change the final result, since the heat effect of Na_2O+O would vary by 19,400^c in both of the calculations below. From the mean of experiments 2 and 3 we have

$2Na_2O_2 + xNa_2O + Bi_2O_3 = (Na_2O)xBi^2O_5 +$ ..... 92·8^c
$2Na_2O + 2O = 2Na_2O_2 +$ ..... 38·8

$xNa_2O + Bi_2O_3 + 2O = (Na_2O)xBi_2O_5 +$ ..... 131·6^c

From experiment 1 we have

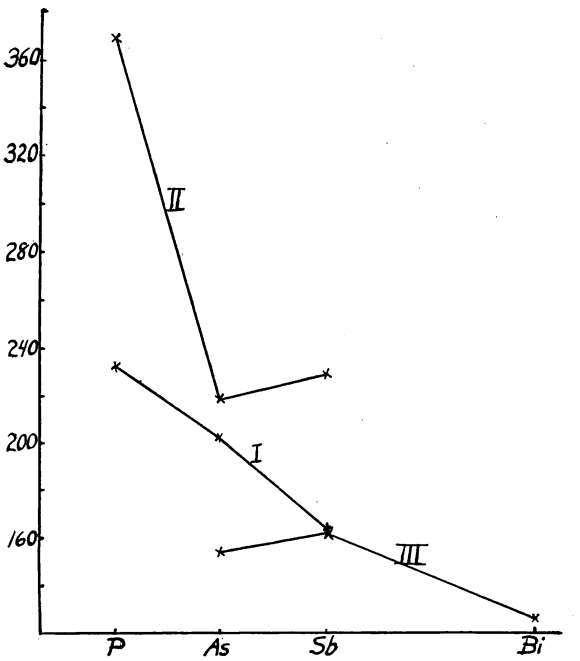
$5Na_2O_2 + 2Bi = (Na_2O)xBi_2O_5 + xNa_2O +$ ..... 170·6
$Na_2O + 5O = 5Na_2O_2 +$ ..... 97·0

$xNa_2O + 2Bi + 5O = (Na_2O)xBi_2O_5 +$ ..... 267·6

The heat of formation of Bi_2O_3 is $267{\cdot}6^c - 131{\cdot}6^c = 136{\cdot}0$. This agrees well with Ditte and Metzner's* result of $137{\cdot}8^c$.

The fusions of the calorimetric experiments left when treated with water a dull yellow product, which after drying

FIG. 1.



at 100° contained a peroxide of bismuth, water and a little sodium. It yielded on heating about half the weight of oxygen required to convert the Bi_2O_3 left into Bi_2O_5, that is, only about one-half of the bismuth in the substance was in bismuthic acid. Several preparations were made by heating a mixture of bismuth trioxide and sodium peroxide, and it was found that the bismuth compound formed gave off oxygen

* C. R., cxv, 1303.

slowly at room temperature and rapidly in hot water, retaining, however, considerable peroxide.

In the figure, atomic weights are plotted as abscissas and heats of combinations as ordinates. The line I shows the heat of the reaction $3Na_2O, R_2O_5$; II of R_2, O_5, and III of R_2, O_3.

We observe that, as the atomic weight of arsenic is nearly the mean of the atomic weights of phosphorus and antimony, so the heat of combination of arsenic pentoxide with sodium oxide is almost the mean of that of the union of phosphorus pentoxide and antimony pentoxide. The heat effect of $3Na_2O, R_2O_5$ is, therefore, closely related to the atomic weights of phosphorus, arsenic and antimony, and not to the affinity of these elements for oxygen. We also observe that the heat of oxidation of arsenic trioxide is nearly the same as that of antimony trioxide to the pentoxide.