Thermodynamics of Dearsenication and Deantimonisation of Copper and of the Reaction Products

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ABSTRACT

The chemistry of the alkaline oxy-compounds of antimony and arsenic are described in relation to the better known chemistry of the corresponding phosphorus compounds. It is concluded that the pentavalent compounds will be formed at equilibrium at high temporaries under very basic conditions. Equilibration runs of droplets of liquid copper and liquid sodium carbonate have been carried out by levitation melting techniques. The results of these experiments are compared with the calculation of the Gibbs free energy changes of the reactions involved. These results are compared with those of other workers.

INTRODUCTION

Much interest has been shown in recent years in the removal of arsenic and antimony from copper by fluxes to avoid problems in electrorefining and to control the fugitive emissions from furnace stacks with resultant pollution. The diminishing availability of high grade ores and the development of the continuous processes make the removal of arsenic and antimony difficult. A number of papers have presented the data obtained in experiments in which liquid copper containing arsenic or antimony have been equilibrated with sodium carbonate slags in laboratory and in industrial fire refining furnaces[1-4]. Some ambiguities exist when these results are compared and it was decided to carry out experiments on levitated drops of liquid copper with attached sodium carbonate slag under conditions where the oxygen potential and CO_2 pressure of the whole system could be rigidly controlled. The results of some of the experiments are discussed below.

It is thought useful to make a survey of the known chemistry of the oxides of arsenic and antimony and to compare them with the much better understood chemistry of the oxides of phosphorus[5] to discover whether the observed high temperature experiments cited can be satisfactorily reconciled with the general body of knowledge about the compounds concerned.

Stabilities of III- and V- valent Group 5 Oxy-compounds

The efficient removal of arsenic and antimony from copper requires the use of a basic slag because although it can be performed to some extent under neutral conditions, the basic process is more efficient. This bears a close relationship to the removal of phosphorus from the metal in basic steel making processes. The effect of basic slag additions is illustrated in Fig 1. The oxidation of arsenic and antimony proceeds very much as that of phosphorus. At low oxidation potentials they are oxidised to the III-valent state and quite high oxygen potentials are needed to convert these oxides to the V-valent ones. In fact As_2O_5 and Sb_2O_5 decompose with oxygen evolution at comparatively low temperatures. (A number of intermediate oxides exist but for the present purposes they can be regarded as merely double oxides of III- and V- valency).

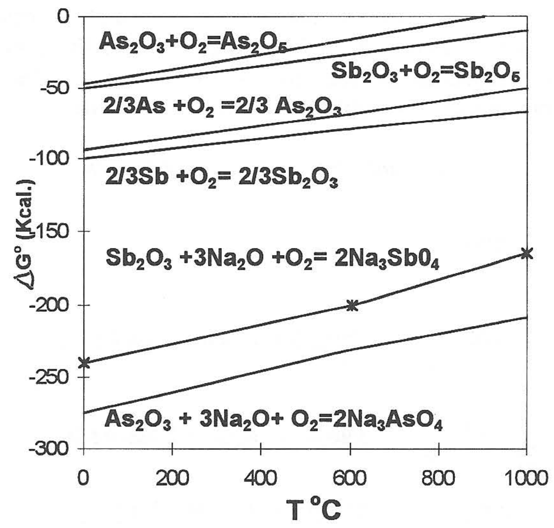

Figure 1 Free Energies of Formation of As and Sb Compounds

The effect of alkali on the stability of the these oxides is dramatic and the formation of alkali metal compounds lowers the activity of the V-valent oxides as shown in Fig 1. The heats of reaction of the III and V-valent oxides of As and Sb in liquid caustic soda at 400°C have been measured by Dougill[6]. The reactions of the V-valent oxides were found to be very exothermic as shown below:

$$1.5Na_2O + 0.5As_2O_5 = Na_3AsO_4 \quad \Delta H^{\circ}_{298} = -104.9 \pm 5.5 kcal.$$

$$1.5Na_2O + 0.5 Sb_2O_5 = Na_3SbO_4 \quad \Delta H_{298} = -81.8 \pm 8.5 kcal.$$

Mixter[7] and Lovchikov[8] have also quoted values in fair accord with these.

This indicates the basis of how the Group V elements are extracted in the Harris process for lead refining.

The reactions of As_2O_3 and Sb_2O_3 with liquid NaOH were found to be complex and the compounds formed could not be clearly characterised. In the case of arsenic, one of the products was metallic arsenic showing that some sort of disproportionation reaction had occurred. The heats of reaction of As_2O_3 and Sb_2O_3 with NaOH were found to be -18 kcal/mol and -6.1 kcal /mol respectively . This is much smaller than that with V-valent compounds which indicates that the stability of arsenites and antimonites are less than the corresponding V-valent compounds.

This is very much in accord with the chemistry of phosphorus compounds[5]. The III-valent oxide is readily oxidised to the V oxide and the higher valency state is stabilized by alkali to form very stable phosphates. Also by analogy with As and Sb the phosphites of sodium disproportionate on heating with the production of phosphates and reduction products such as elemental phosphorus and phosphine gas.

The analogous behaviour of P, As and Sb in these respects is illustrated in Fig 2 when it is seen that there is a sequence of stabilities of the V-valent sodium compounds. The stabilities decrease in the order:

phosphates>arsenates>antimonates.

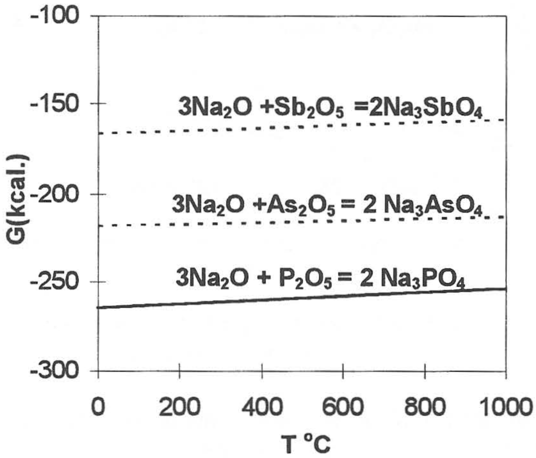

Figure 2 Relative Stabilities of Na_2O with P_2O_5, As_2O_5 and Sb_2O_5

Because of this behaviour, it was considered useful to construct a heat of mixing diagram for the various Group 5 oxy-alkaline compounds, Fig. 3 is based on the known results for sodium, ortho-, pyro-, and meta-phosphates measured by Meadowcroft and Richardson[9]. The values of ΔH^o_{298} for sodium-orthoarsenate and orthoantimonate are measured ones and the dotted lines are sketched in by analogy with the phoshates for the pyro- and meta- compositions. The entropy changes for reactions between solids to produce solids are small[10] so that to a fairly good approximation $\Delta H^o_{298} \cong \Delta G^o_T$. Changes due to melting involve relatively small heat effects but the vaporisation of P_2O_5 requires a change in the zero point to that indicated in Fig 3, point X.

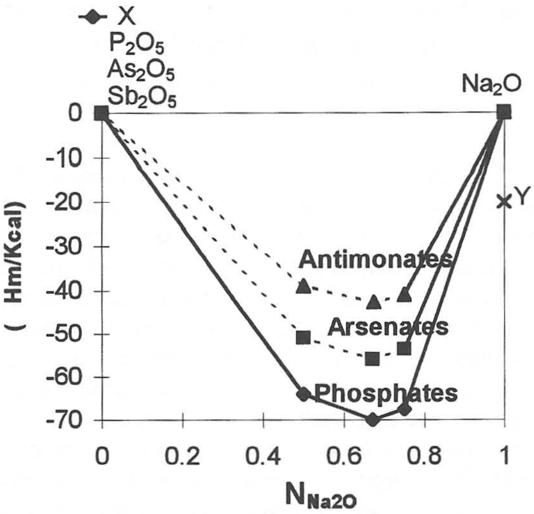

Fig 3 Free energies of Mixing Na_2O with P_2O_5, As_2O_5 and Sb_2O_5

It is clear from this diagram that in the presence of Na_2O at unity activity, (or at an activity of about 10^{-3} as in Na_2CO_3 at 1200 °C in the presence of 1 bar pressure of CO_2 , Point Y) the ortho-compounds should be formed and the activities of As_2O_5 and Sb_2O_5 will be very low, of the order of 10^{-40} and 10^{-30} respectively. For further information on the thermodynamics of such polyanionic compounds see Richardson[11].

PRESENT WORK

A survey of the work carried out by other investigators showed that considerable discrepancies exist between their results as shown in figures 4 and 5 which are plots of log of the partition coefficient $P = (\%As, Sb \text{ in slag})/[\%As, Sb \text{ in metal}]$ against $-\log P_{O_2}$ (bars). One reason for this was considered to lie in the difficulties of controlling the metal-slag-gas interactions so that true thermodynamic equilibrium was set up throughout the system. The difficulties arise from the complexity of the reactions involved; overall the reaction can be written as :

$$[As,Sb]_{Cu} + 3/2Na_2CO_3 + 3/4O_2\ g = Na_3[As,Sb]O_4 + 3/2CO_2\ g \quad (1)$$

where the standard states are 1 wt % solution in liquid copper, pure liquids or solids and gases at 1 bar pressure at the temperature considered.

The overall equilibrium of a system depends on maintaining good mixing of the condensed phases and control of the oxygen *and* the CO_2 pressures of the gas phase at the temperature considered.

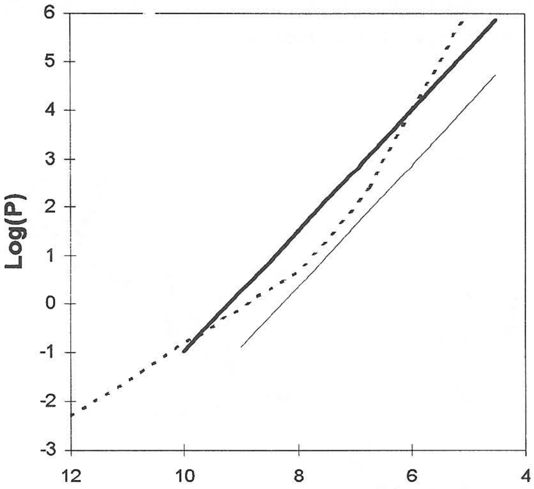

Figure4 Published Results For Arsenic

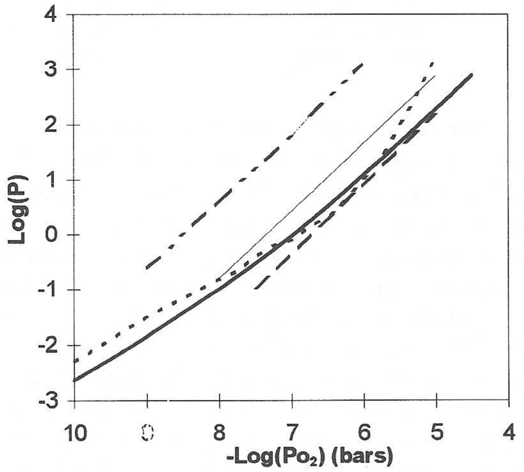

Figure 5 Published Results for Antimony

Some of the experiments described in the literature were carried out by adjusting the oxygen content of liquid copper by Cu_2O additions to the metal in a crucible. The slag floating on top will react with the [As,Sb] with the evolution of CO_2 at the interface. This will generate a high but uncontrolled oxygen potential at the slag-metal interface. The absence of this gas later in the experiments will make the reverse reaction difficult and imperil proper equilibrium, where only the top surface of the slag is contacted with CO_2 or Ar gas. The slag/gas interface is then subjected to different conditions from the those at the metal/ slag interface.

Sampling methods appear to have posed some problems. Chilling the crucible followed by sectioning and sampling may introduce segregation errors. Some entrapment of metal droplets in the slag when gas bubbling was used has been mentioned.

With these considerations in mind we decided to carry out experiments by levitation melting of copper droplets with slag attached by surface tension in a fast moving stream of CO_2-CO-Ar gas, where experience of this technique has shown that good slag/metal/gas equilibrium can be achieved[12].

The principal advantages of this method are:

1. Thorough mixing of metal and slag phases
2. Rapid attainment of equilibrium (In the present case CO_2 evolution at the slag metal interface ceased after about 30 seconds).
3. Good metal/gas , slag/gas and slag/metal contact
4. Rapid quenching of samples at the end of run. (Both phases solid within 2 seconds)
5. Whole samples analysed, avoiding segregation problems.
6. Absence of crucible contamination

To this, may be added the mundane fact of cheapness of the operation since no crucibles are used !

The disadvantages of the method are:

1. Temperature control is difficult and requires considerable skill, using a radiation pyrometer focused at the top of the metal droplet
2. Samples of metal and slag are small, (0.2 - 1g)

The apparatus used was essentially the same as that used by Katyal[13]. At one time it was thought that the slag would be appreciably cooler than the metal so that true isothermal metal/gas equilibrium would not be achieved. This was thoroughly tested out by Taylor[12] who obtained the same results on the Cu,Ni/FeO.SiO_2 system as had been obtained by conventional crucible experiments.

In the present experiments the copper alloys containing about 0.5 wt% of [As,Sb] were levitated by raising the sample on a silica platform into the coil. When the metal was hot but not molten, anhydrous sodium carbonate was attached to it from a platform. (The sodium carbonate had been premelted and cast in copper mould and stored in a furnace at 200°C). The temperature was raised and stabilized at 1200°C by controlling the R.F generator power. Quite an art is involved in securing a suitable slag layer and this was found more difficult in the case of As containing metal than with Sb. The well known surface active properties of As in liquid copper were probably responsible.

All the experiments were carried out in the a stream of CO_2/CO or $CO_2/CO/Ar$ gas with CO_2/CO ratios ranging from 8 to 1800 passing down through the silica tube at about 1800 Nml/min, which experience has shown was sufficient to avoid problems due to thermal segregation at the temperatures involved.

As soon as the metal melted, a vigorous evolution of CO_2 occurred forming a sort of beard of bubbles around the reacting system at the slag metal interface. This disappeared after about 30 seconds. Experiments in duplicate carried out for varying times showed that the metal /slag/gas equilibrium was achieved in less than 1 minute; although the runs were normally continued for 20 minutes.

The metal and slag samples were analysed by atomic absorption spectrophotometry. Hydride generation was also used for metal samples of low As and Sb content. Mass balances were carried out by weighing the metal and slag before and after each experiment.

On account of the small slag samples involved (0.08g) it was thought that ±5% of the total recovery of the [As,Sb] was satisfactory evidence of the soundness of the handling and analytical procedures involved. This was achieved in many of the Sb runs, indicating that little Sb had been lost by vaporisation.

In case of As , however, the mass balance results were very much more erratic and on occasions losses of 20% or more of the initial arsenic were observed. Slag additions and recovery from As containing droplets, mentioned above were difficult and this may have affected the mass balance results but it is now thought that variable losses of As by vaporisation may have occurred as discussed below.

EXPERIMENTAL RESULTS

Antimony

The results of 30 runs in the oxygen partial pressure range of 10^{-10} to 10^{-5} bars and distribution coefficients from 0.01 to 258 are given in Fig. 6. Our principal interest lay in the removal of As and Sb to very low levels so that initial alloys containing about 0.5wt% of the respective impurity were used. The metal and slag analyses after equilibration lay between 0.46-0.006 wt% and 0.009 -1.5 wt% in the metal and slag respectively.

The best fit line (Line A) drawn through the experimental points has a slope of about 3 which was unexpected because as stated above, it was considered that under highly alkaline conditions Sb would form V-valent compounds in favour of III-valent ones. Other researchers have also found a variety of slopes for their experimental results.

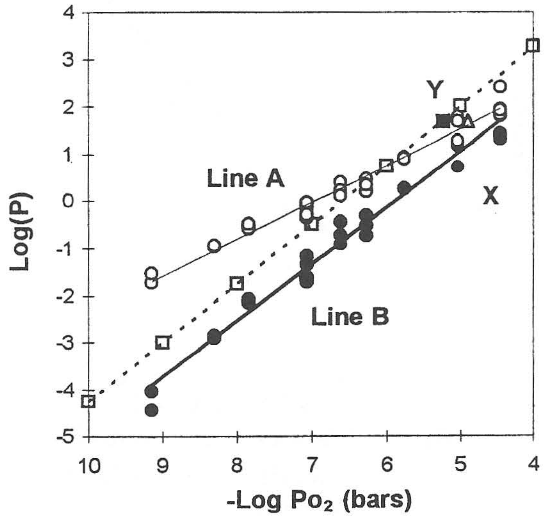

Figure 6 Antimony Run Results

Further consideration showed that one should only expect a slope of 5 for the plot of log partition coefficient against log Po_2 if the activity coefficients of the condensed phases remain constant. This is a reasonable assumption for $\gamma[Sb]_{Cu}$, if 1 wt% is used as the standard state and would be so for the Na_3SbO_4 if it were present as a standard pure solid phase. The extensive work of Taskinen et al[14], indicates that Na_3SbO_4 is soluble in liquid Na_2CO_3 to the extent of $X\ SbO_{2.5} = 0.04 \pm 0.01$; Na_3AsO_4 was shown to be soluble to the extent of $X\ AsO_{2.5} = 0.03 \pm 0.01$. These figures correspond to 4.5 wt% Sb and 2.1 wt% As in slag respectively.

On the assumption that our results for Sb in slag, which all fell below the 4.5 wt% indicated a Henrian solution from 0-4.5 wt% Sb, the results of Fig 6 were corrected to a constant value of 4.5% Na_3SbO_4 i.e. the saturation limit of Na_3SbO_4. The line B drawn through the points now showed a slope of 4.8 between log partition coefficient against log Po_2 indicating that V-valent Sb was produced. This agreed with the prediction on thermodynamic grounds given above and with the findings of other investigators.

Arsenic

The results of 18 runs in oxygen partial pressures similar to those used in Sb experiments in are given in Fig 7. The slope of the best fit line (Line A) through these points was close to 4, implying a mixture of the III and V-valent arsenic compounds. The slag analyses below 2.1wt% were considered to represent As in solution as in the case of Sb. They were thus corrected to the 2.1 wt% As with pure crystalline Na_3AsO_4 as the standard state. The slope of the best fit line, B, was 4.6, closer to that expected for V- than the III-valent compounds.

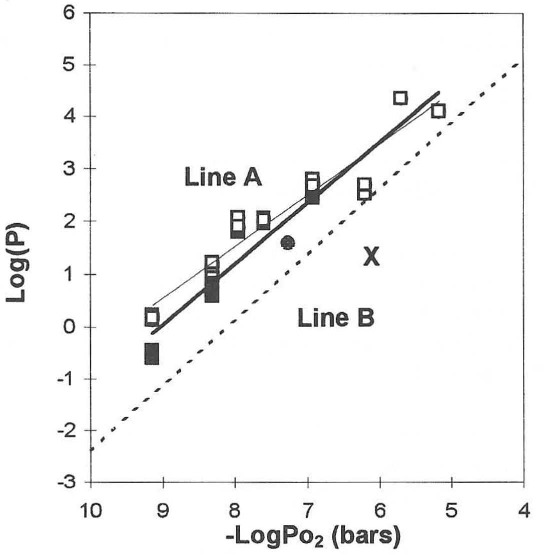

Figure 7 Arsenic Run Results

The scatter of the As results was greater than the Sb ones and it is considered that this may be associated with the loss of As from the system as mentioned above.

A possible explanation for this loss could be the vaporisation of $NaAsO_3$ analogous to that of $NaPO_3$, which fumes violently when heated to about 1000 °C. It is thought that this could be briefly produced at the metal/slag interface where the rapid reaction, between the newly released As and the slag , as the metal is melted, forms a boundary layer in which arsenic oxide counter-diffuses with Na_2CO_3 forming a graded meta-/pyro-/ortho- region (Fig 8). The evolution of CO_2 in this region could accelerate the loss of meta-arsenate by vaporisation. Alternatively it may be that the rapid oxidation of arsenic from the metal may result in the transitory formation of As_2O_3 which is volatile at these temperatures.

Evidence to support the former has been obtained in DTA/TG experiments which will be fully described elsewhere. It was found that the sodium pyro-arsenate suffered a severe loss in weight above 1000°C which was consistent with the reaction:

$$Na_4As_2O_7 = Na_3AsO_4 + NaAsO_3\uparrow$$

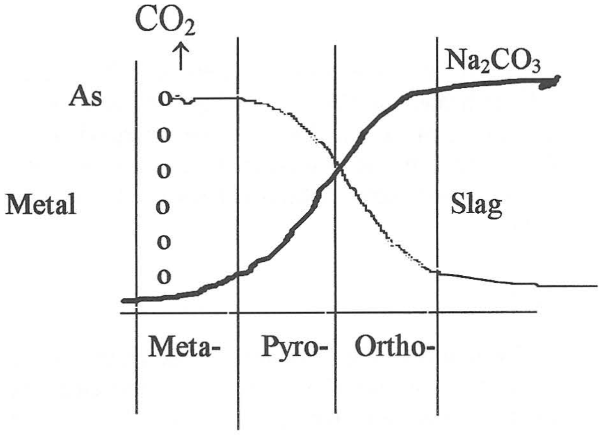

Fig 8

Another test carried out with sodium pyro-arsenate in the presence of an excess of Na_2CO_3 showed no such large weight loss.

It is interesting to note that in the industrial fire refining of copper using Na_2CO_3 a substantial amount of As is lost up the stack by vaporisation[15] and this may be due to one of the mechanisms described above.

DISCUSSION

Antimony

In Fig 6 the Sb runs corrected to the standard state of pure crystalline Na_3SbO_4 give a slope of 4.8 which indicates within experimental error that V- valent Sb is produced under the very basic conditions of the experiment. The data produced by several authors seem to show changes in slope of the plot of Log (P) against log Po_2 over a range of oxygen pressure of 10^{-12} to 10^{-5} bars. These have been attributed to the changes in valency of Sb from V- to III-. All our experiments were carried out at less than the saturation limit of Na_3SbO_4 in Na_2CO_3 but we would have expected a discontinuity in the experimental graph line had the solubility been exceeded, as was observed by Kojo[14].

A calculation of ΔG^o_T for reaction 1 was carried out *ab initio* as shown in the Appendix. This gives a value of $K = 8.2 \times 10^4$ at 1200°C. If all reactants and products were in their standard states, this would indicate that the oxygen pressure of 1.2×10^{-5} bar would result. In terms of distribution coefficient, the presence of 1 wt% Sb in copper and 47.8% Sb (the hypothetical standard state) in the slag gives Point X, the value of log P against $\log P_{O_2} = -4.92$. The line drawn through point X at a slope of 5 lies close to that for our results corrected to solid Na_3SbO_4 standard state.

Completely independent calculations by Themelis et al[16] indicates the Point Y in Fig 6. In view of the cumulative errors involved in the thermodynamic calculations, it is considered that satisfactory agreement has been achieved between theory and practice

Arsenic

The results of the runs were not as satisfactory as the Sb runs in that they were more scattered and erratic and that sometimes large losses of As occurred. Point X in Fig 7 was derived in a similar way to that for Sb in Fig 6, using the data listed in the Appendix. There is fairly satisfactory agreement between theory and practice.

Not shown in Fig 7 are an erratic set of values at high oxygen potentials. These were carried out at CO_2/CO greater than 1500/1 and it may be that such a gas mixture fails to reach the proper oxygen potentials at the slag metal interface because of the scarcity of CO molecules at the interface. This problem is a being investigated further.

CONCLUSIONS

The levitation method of studying metal/slag/gas equlibria has been applied to the purification of As and Sb from liquid copper by sodium carbonate in CO_2/CO and $CO_2/CO/Ar$ gas mixtures.

The results show that both these metalloids are oxidised to the pentavalent state under very basic conditions, at high temperatures.

This conclusion is in accord with the general body of chemistry of the oxidation of the Group 5 elements.

Further work on the systems is being carried out.

ACKNOWLEDGMENTS

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Appendix

REACTION	ΔG^o (cal.)	Ref.
4/5 [Sb] = 4/5 Sb l	+ 10 000 + .32 T	17
4/5 Sb l = 4/5 Sb s	- 3,800 + 4.21T	18
4/5 Sb s + O_2 g = 2/5 Sb_2O_5 s	- 96320 + 45.74T	18
2/5 Sb_2O_5 s + 6/5 Na_2O s = 4/5 Na_3SbO_4 s	- 65440 + 0 T	6
6/5 Na_2CO_3 1 = 6/5 Na_2O1 + 6/5 CO_2 g	+ 90 730 - 37.52 T	17
6/5 Na_2O 1 = 6/5Na_2O s	-14670 +10.81 T	18
4/5 [Sb] + 6/5 Na_2CO_3 1 + O_2 g = 4/5 Na_3SbO_4 s	- 79, 500 + 31.56 T	
4/5 [As] = 4/5 As l	+11127.2 + 8.06 T	19
4/5 As l + O_2 g + 6/5 Na_2O s = 4/5 Na_3AsO_4 s	- 170 915 + 42.27 T	8
6/5 Na_2CO_3 1 = 6/5 Na_2O1 + 6/5 CO_2 g	+ 90 730 - 37.52 T	17
6/5 Na_2O 1 = 6/5Na_2O s	-14670 +10.81 T	18
[As] + 6/5 Na_2CO_3 1 + O_2 = 4/5 Na_3AsO_4 s	-83 727.8 + 23.62 T	