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A SCIENTIFIC INVESTIGATION

OF

CHINESE PROTOCHEMISTRY

A Thesis

presented for the degree of

MASTER OF SCIENCE

in the Faculty of Science of the

University of St. Andrews

by

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St. Andrews

January 1983.

Th 9808

DECLARATION

I hereby declare that this thesis is a record of the results of my own experiments, that it is my own work, and that it has not previously been presented in application for a higher degree.

The research was carried out in the Chemistry Research Department of the University of St. Andrews, Scotland under the supervision of Dr. A.R. Butler and Dr. C. Glidewell.

CERTIFICATE

I hereby certify that Sharee E. MacKerron has spent six terms at research work under my supervision, has fulfilled the conditions of the University Court 1974 No. 2 (St. Andrews) and she is qualified to submit the accompanying thesis in application for the degree of Master of Science.

Director of Research.

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ABSTRACT

This thesis reports a scientific investigation into the work performed by the early Chinese alchemists. The results, as well as being of modern scientific interest, serve to prove that what is written in these alchemical treatises is accurate and can be taken seriously. It also gives an insight into some of the equipment and techniques used during the sixth century in China. Some of the less well-known advances of the Chinese civilisation are highlighted and major differences between science and technology in East and West are emphasised.

In Chapter 1 the best approach was believed to be an experimental comparison of various ancient and modern stills. This showed how efficient the most characteristic East Asian still called the Chinese still was compared to others.

A theoretical approach was found to be most appropriate in Chapter 2 which concerned the possibility of smelting of aluminum in medieval China. The conclusions reached were verified by archaeological and analytical work done elsewhere.

The preparation of mosaic gold (tin (IV) sulphide), perhaps one of the most significant reactions to the Chinese alchemists, was studied in detail in Chapter 3 and the results allowed a new reaction scheme to be proposed. Various evidence was collected to support this scheme. As a consequence of this experimental investigation the translation of an ingredient in an alchemical recipe was inferred.

Finally in contrast to the preceding chapter, Chapter 4 deals with a problem in inorganic solution chemistry, and points out reactions which previously have enjoyed little attention. At the same time it gives a deeper understanding of the Chinese alchemical recipes that describe the methods used to bring solids into aqueous solution.

INTRODUCTION

The Chinese alchemist lived in a feudal society where scholars enjoyed a high social standing. Less highly regarded were the farmers and artisans who in turn commanded more respect than merchants. The alchemists were perhaps not strictly regarded as scholars since unlike the astronomers who provided knowledge of practical importance, their discipline was closely bound up with Daoism, a system of philosophy and religion. Daoism focussed on the problem of mortality, the Daoists wished for long life and so the disciples were led to the study and practice of alchemy in order to achieve this aim. The emphasis in Chinese alchemy was base metal to gold transmutation similar to European alchemy. However Chinese and European alchemy were far from identical in that gold to the Chinese was not a medium of currency but an imperishable substance. It was believed by the alchemists that eating and drinking from vessels made of artifical gold could prolong life, a far nobler use than that of commercial pursuits.

These Daoist philosopher alchemists had little respect and interest for the feudal system which is perhaps why Wei Bo-yang who has been called the "father of Chinese alchemy", is reported to have favoured the seclusion of the mountains with three disciples to conduct his experiments. There he sought after the secret for making the golden elixir of immortality.

Another well known Daoist called Ko Hung (280-360 A.D.)

wrote an alchemical manuscript called Bao-pu zi (Book of the Preservation of Solidarity Master) in which he gives numerous recipes for transmutations and for preparing elixirs of immortality made from metals and minerals. Certain minerals were regarded as substances from which potent elixirs might be made and several manuals describe methods for bringing a number of minerals into solution, which also demonstrates the appearance of the chemistry of inorganic reactions in aqueous medium in sixth century China. The Chinese alchemists had an affinity for keeping meticulous records and in view of the advanced state of their technology at this period one may expect to be able to repeat some of these experiments.

With the advantage of knowledge of modern theories and the use of modern equipment it should be possible to elucidate some of the alchemical recipes. This was the aim of this investigation.

Some of the difficulties encountered, such as loss of information through translation, could not be overcome. However even with a clear translation it was not always obvious exactly which chemical was meant. This is shown in Chapter 3 in the translation of han yen as meaning 'cold salt'. Some of the alchemists also did not present 100% of the information. A further difficulty lay in simulating the experimental conditions since many of the Chinese experiments were performed over periods in excess of thirty days. We did not carry out our experiments

for this time scale and therefore could not expect the magnitude of the effects to be so great. The purity of modern chemicals was too high in some cases, since as can be seen in Chapter 4, it was often an impurity which was the key to the reaction.

Finally, the nature of this thesis differs in many respects from a normal scientific presentation and accordingly it has been written in a manner to present both scientific and historical information together.

CHAPTER 1

An Experimental Approach to the History of Distillation

The process of distillation¹ is a commonplace part of laboratory procedure, and an essential tool in industry. Little thought is given to its history. It is in fact one of the most ancient of the chemical arts and the discovery of many of the principles of distillation far antedates the dawn of exact science. The beginnings of the distillation art are lost in the mist of antiquity. In the third century B.C., Aristotle knew that sweet water could be made by evaporating salt water and condensing the steam. In the first century A.D. Dioscorides hung flocks of wool in the vapours of boiling liquids and by wringing out the wool secured the distillates. Whether these were just observations of certain conditions and events which had great significance to them but which, in fact, they did not fully comprehend and understand, or whether distillation in the present sense of the word was known to them is one of many basic questions. Certainly Liebmann² leaving legend, hearsay and speculation aside and confining himself purely to established and documented facts was led to believe that distillation in its present day sense was not known in antiquity. Although the word "distillare" can be found in a number of places he emphasises the interpretation of distillation as used not only by the Greeks and Romans, but perhaps even before them by the Arabians, is confused with what later was recognized and what we now understand as sublimation. The study of distillation is inseparably connected with the history of alcohol, which as a medicine and stimulant was known in very early times but only as a mysterious and unknown constituent of readily available natural products. Of these wine was the most

prominent. Techniques for the distillation of wine to give strong spirituous liquor was developed in several civilisations.

Although the aim was the same the structure of the stills differed. The evolution of Western Stills has been treated by Berthelot³ and Taylor⁴. The alchemical books of the sixteenth and seventeenth centuries are replete with representations of distillation equipment⁵, some of them quite complex and showing in their design great ingenuity. The important improvement represented by water cooling in the West seems to be reserved to a Swiss scientist, Gessner, born in Zurich in 1516, previously condensing relied solely on air cooling. It has been suggested,⁶ that the introduction of water cooling was a critical factor in the development of alcohol distillation. It is curious that the East Asian types of stills, the Mongolian and Chinese stills, had never been taken into consideration before Needham's⁷ study in the classical theories of the still. Although the filiation of modern chemical apparatus with its medieval antecedents back to the equipment of the Alexandrian proto-chemist has been traced by many writers, after reading the topic of the development of stills⁷, it is perhaps a misapprehension to think that the East Asian still types play no part in modern chemical technique, and that all stills are descendants of those of the Greeks. Distillation has been known in the East from a very early period, but it is again difficult to trace it to its sources. In China, distillation first appears in connection with alchemy. The Chinese alchemists employed their distillation apparatus in the preparation of

mercury, roasting cinnabar (mercury (II) sulphide) and decomposing their oxides of mercury. Who discovered strong distilled alcohol, and where, has been previously discussed.⁸ It is stated⁹, that as in the West, the distilling of spirituous liquors cannot be dated earlier than 1100, although in the light of all the other evidence^{7a} further distillation of alcohol in China, the sixth century A.D. would seem not too early.

The Mongolian and Chinese simple still types are distinctly different from the Mediterranean types and cannot be explained as related or derived from them. The efficiency of each type of the basic still is relevant to the discussion and will add considerable interest.

Thus the four basic forms of the simple still, which are described in more detail by Needham^{7b} are as follows;

- (i) The "Mongolian" still, where the vapours from a boiling liquid are condensed on the concave roof of the still and fall into a central catchbowl.
- (ii) The "Chinese" still, which is similar to the Mongolian still, except that the catchbowl is provided with a side tube conveying away the distillate into a receiver, so that the distillate can be continuously removed.
- (iii) The "Ghandhāran" (Indian) still, which is really a retort; condensation occurs in a cooled receiver.
- (iv) The Hellenistic still where condensation occurs on the walls of the still and collects in a circular gutter, which is provided at one point with a side tube leading off.

An essential in many distillations is the separation of the distillate into portions of different volatility. Present day fractionating apparatus secures this separation by refluxing the distilled vapours as they arise. Heavier portions are continuously returned to the still by partially condensing the vapours in a tower from which, at the same time, several streams of distillate of different properties are withdrawn. These vapours are condensed fractionally into a series of receivers. As is noted from the description of the still, these practices are not new.

A previous study was carried out¹⁰ using glass models of these stills. The efficiency of the preparation of strong spirituous liquors from a fermenting broth was simulated by distilling a dilute aqueous ethanol (7.5% wt/wt) solution. From the observations it was found that the preparation of strong spirituous liquors was, from a technological point of view, a rather simple matter and no civilisation had a distillation apparatus which gave it an advantage. Even the most primitive of stills (e.g. the Mongolian still) will yield strong spirituous liquor. Thus the unusual properties of an alcohol-water mixture which allow the alcohol to be concentrated so readily, prevented any real comparison of the efficiency of the different stills. The anomalous properties of ethanol-water mixtures have been described in detail by Frank and Ives.¹¹

To compare the stills we turned to a binary mixture of two liquids which is more regular than ethanol-water, making the degree of separation a more sensitive probe for an assessment of

the efficacy of the stills. Glass working models of two of the basic forms of the simple stills were constructed, the most characteristic East Asian still called the Chinese still and the Hellenistic still. The external dimensions of the stills were identical so as to permit precise comparison. The mixture we chose was ethyl acetate (b.p. 77°C) and n-butyl acetate (b.p. 126.5°C) as esters of carboxylic acids, they are related to the essential oils which have been distilled in all civilisations (the West, Arab and Chinese). The distilling of essential, vegetable oils and petroleum oils was carried out by the Arabs and Byzantines before alcohol distillation started in the West. Although as should be pointed out, the same sequence may not have occurred in China, since so far as can be seen, Chinese stills had an effective cooling device from the beginning. Therefore, it may be that the essential oils followed alcohol, instead of preceding it, as they did in the West. All that we can state with certainty is that the distillation of essential oils was carried out in the Chinese culture-era.

This liquid mixture be distilled was contained in a 250 ml round bottom flask, attached to the still by a ground glass joint. The source of heat employed was an electric mantle with a rheostat. The volume of water used as coolant was 50 ml in both cases. In each experiment 50 ml of a 50:50 (vol/vol) mixture was placed in the flask and heating commenced. Initially aliquots of 5 ml were collected but to give a more detailed picture this was changed to 2 ml aliquots. These were analysed by gas-liquid

chromatography, carried out on a Pye 104 chromatograph equipped with a flame ionisation detector. The column, a general purpose one (N.P.G.S.) was operated at an oven temperature of 82°C. Both components of the mixture being near neighbours in a homologous series, are separated with respect to boiling point, the more volatile coming through first. One seeks to obtain chromatographic results in the minimum possible time, and as the resolution factor R for the two substances is greater than 1.5 ie there is baseline separation between components, this can be achieved successfully without degrading the results by increasing the carrier gas velocity to an appropriate flow rate, and subsequently reducing the analysis time. After establishing the optimum operating conditions, an amount was injected to just below the surface of the column packing using a 10 μ L Hamilton syringe.

Absolute calibration is the surest means of quantitative analysis, the standard calibrant used was a 50:50 (vol/vol) mixture of ethyl acetate/n-butyl acetate. The relative amounts of esters in each aliquot were determined from the areas under the appropriate peaks. The amount of each component in the sample mixtures was reported as a volume percentage.

As a source of reference the mixture was first distilled using a modern distillation apparatus with a Liebig condenser. The results are shown in figure 1 where the ordinate is the percentage by volume of ethyl acetate (the lower boiling component) within the aliquot and the abscissa is the total volume of distillate. The final volume of distillate should be 50 ml,

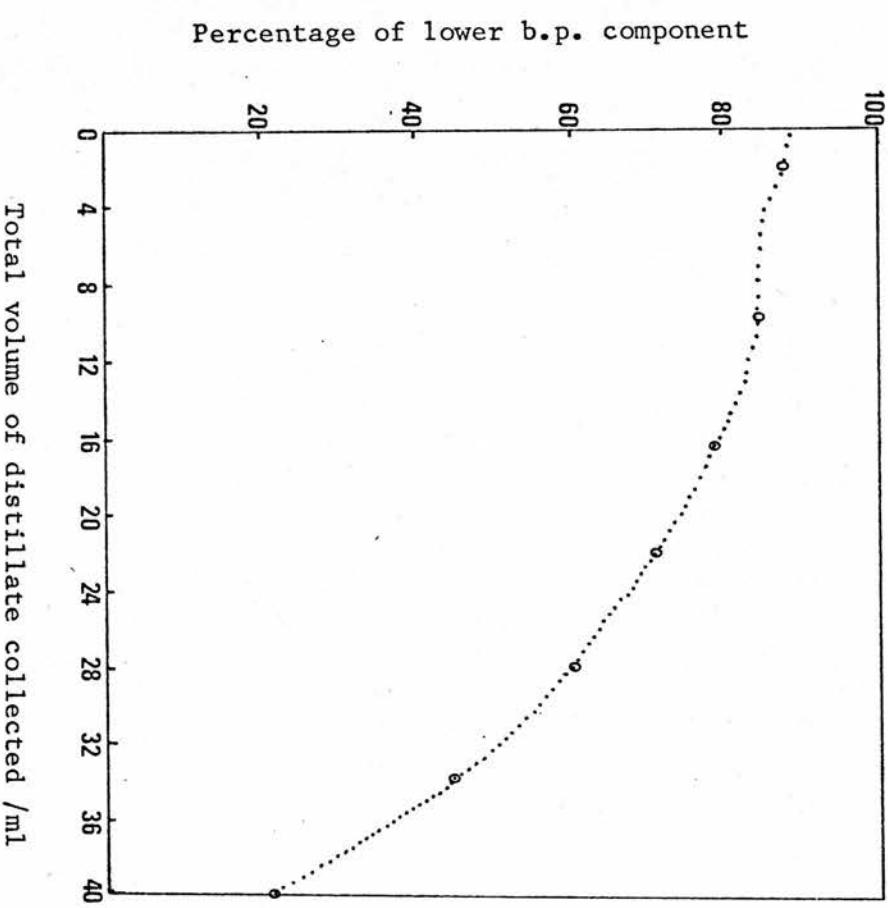


Figure 1 : Distillation of ethyl acetate, n-butyl acetate mixture using a modern Liebig condenser apparatus

but there is hold up in the apparatus and, in general, the distillation was continued until 40 ml of liquid had been collected. Clearly the separation of the esters was very poor, and even a small volume of either ester in a pure state was not obtained. The composition of the vapour and hence, of the distillate depends very largely upon the vapour pressures of the two components in the mixture. In this case the vapour pressures at any one temperature do not differ greatly.

In modern industrial apparatus the degree of success in separating a mixture by distillation is closely related to the inherent efficiency or effectiveness of the column and packing or "plates". Such concepts as height equivalent of a theoretical plate (H.E.T.P.), plate efficiency, height of a transfer unit (H.T.U.) are used in expressing this inherent separating power of the apparatus. This information can be obtained from experimental data of a suitable binary mixture for which the vapour liquid equilibrium diagram is well established. However, if the condensate is divided i.e. there is a change of composition in the still as the distillation progresses the system is said to be operating under partial reflux. In such cases columns are not usually rated by the number of theoretical plates, partly due to the problem of taking duplicate samples from the still and distillate, and because of the changing composition of the still and product liquids with time. Instead consideration of other variables is made such as reflux ratio and hold-up. Reflux ratio is defined as the ratio of moles of reflux liquid per unit time to

moles of product per unit time. Thus a high reflux ratio would mean a large amount of reflux liquid for a given amount of product and in general a better separation. During any time period, a certain amount of liquid introduced into the apparatus is actually in the column as reflux and **rising** vapour and this is known as hold-up.

One of the major factors affecting the sharpness of separation is the proportion of condensate returned. What characterises a modern laboratory distillation apparatus is that there is only a short distance between the boiling liquid and the side arm. All the vapours that pass into the side arm ~~are~~ condensed and none returns to the distillation flask. Another way of stating this is that the system is not operating under even partial reflux. From the equilibrium relationship between vapour composition and liquid composition, the concentration of vapour which a given liquid will evolve under specified conditions of temperature and pressure is fixed. However in most cases this difference in concentration between vapour and liquid is unsatisfactory for accomplishing the separation desired in a single step, as was found to be the case with this distillation of the ethyl acetate/n-butyl acetate mixture. As a result of this poor efficacy, industry in general resorts to the use of the fractionating column which operates under almost complete reflux allowing a better separation than could easily be obtained in a single distillation. In a fractionating column a liquid rich in the volatile component flows down the column and vapour poor in

that component flows up the column. Vapours and liquids are in close contact in such a counter-current apparatus.

Therefore an obvious further experiment, the distillation of ethyl acetate/n-butyl acetate mixture using a modern apparatus with vigreux column, was carried out. The column length was chosen so that it compared closely to the dimensions of the Chinese and Hellenistic stills. The results are shown in figure 2. A better separation is achieved with the vigreux column, although compared to the apparatus with a Liebig condenser, the difference in terms of efficiency is not very large.

After confirming the poor efficacy of a conventional, laboratory, distilling apparatus in the separation of the ester mixture the question arose of where in terms of efficiency the Chinese and Hellenistic still fall, compared with the laboratory, distilling apparatus and the more efficient industrial counterpart with its fractionating column.

The same mixture was examined initially in the Chinese still under the experimental conditions previously described (figure 3). The separation achieved was dramatically improved compared to the modern apparatus with a Liebig condenser and the separation was also better than that achieved with the use of a vigreux column (figure 2). Clearly the distillate condensing after 32 ml of material have been collected in the Chinese still is almost pure n-butyl acetate (the higher boiling ester), although none of the ethyl acetate was obtained in a similarly

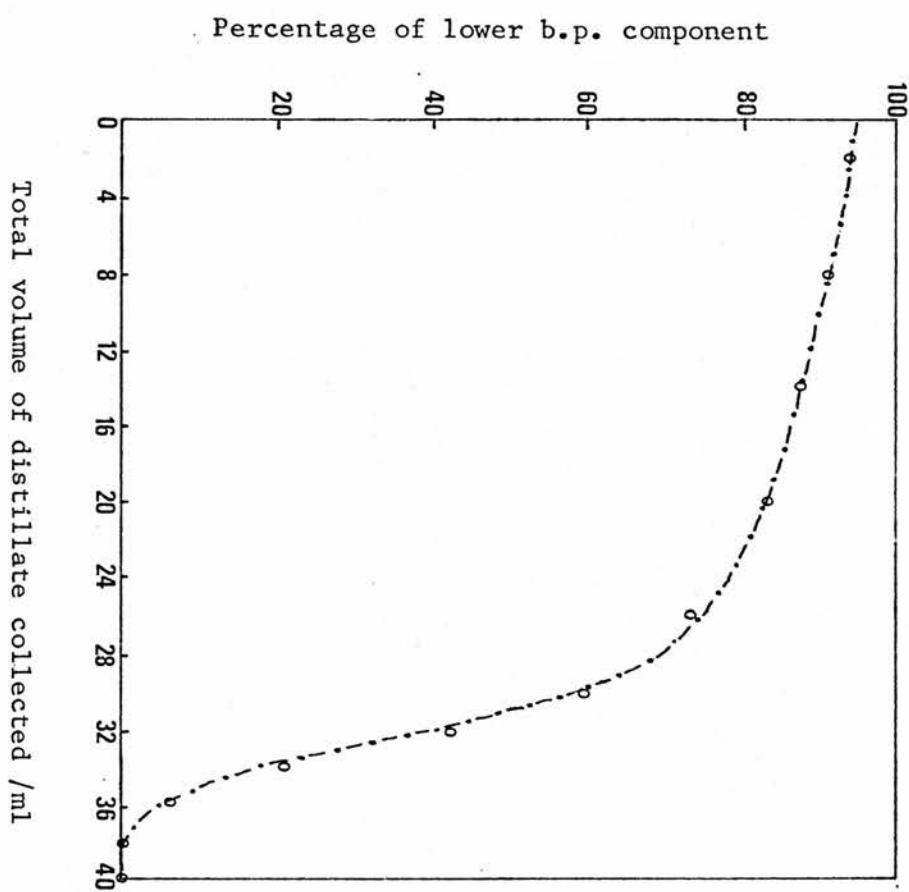


Figure 2 : Distillation of ethyl acetate, n-butyl acetate mixture using a modern Liebig condenser plus vigreux column

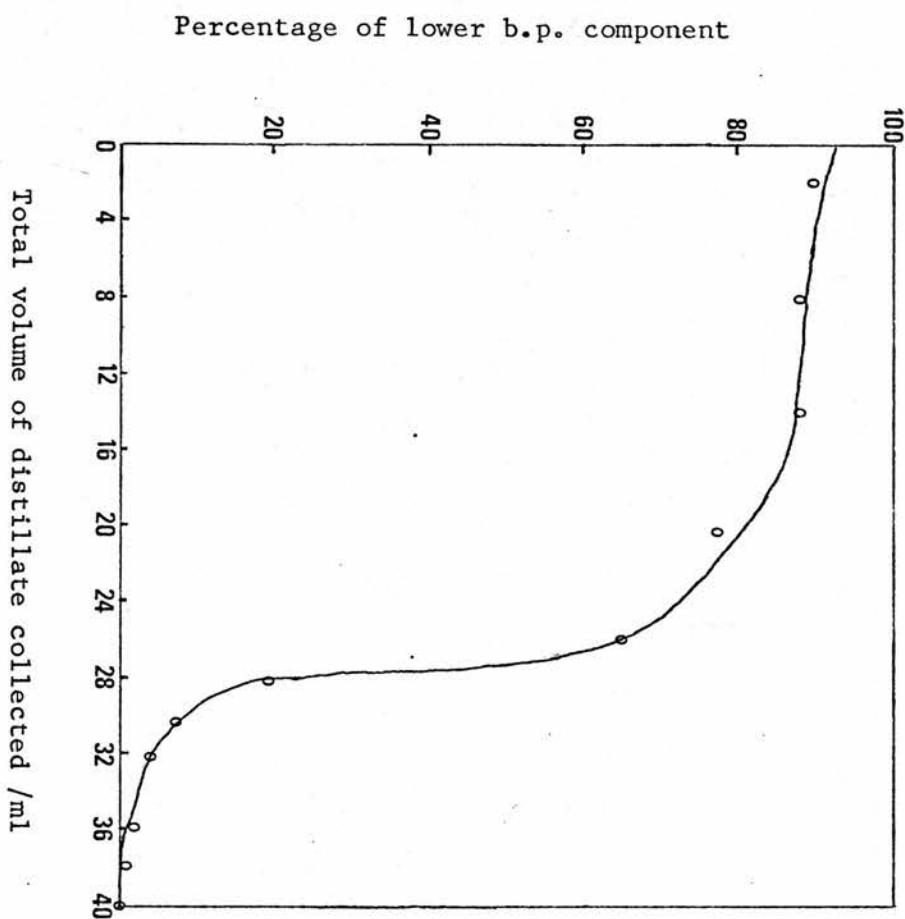


Figure 3 : Distillation of ethyl acetate, n-butyl acetate mixture using a Chinese still

pure state. The reason for the superior efficacy of the Chinese still, compared to the Liebig condenser, is that it is working under partial reflux and liquid resulting from condensation of vapour is in contact with vapour before it passes out of the refluxing system. Thus the vapour, poor in the more volatile component, flows up the column and the liquid rich in that component, flows down the column. As a result of bringing vapours and liquids into intimate contact in the apparatus, the vapours at each point in the column tend to approach equilibrium with the liquid at that point, thereby enriching the vapours at the expense of the liquid. Therefore as the vapour ascends it is enriched in the lower boiling component. That part of the vapour which is condensed and runs towards the central catchbowls is quickly removed from the refluxing system. That which condenses and runs down the outer walls of the still yields some of its ethyl acetate to the ascending vapour, while it is enriched with n-butyl acetate. Although the Chinese still exhibits greater efficacy in separation, than a modern distillation apparatus with a Liebig condenser and that with a vigreux column, the collection of distillate is much slower. The results for a similar experiment with a Hellenistic still are shown in figure 4. There are two points of interest.

First there is a peculiar peak in the composition of distillate around 26 ml. The experiment was repeated a number of times and the same result was obtained. The repeat run results are shown in table 1.

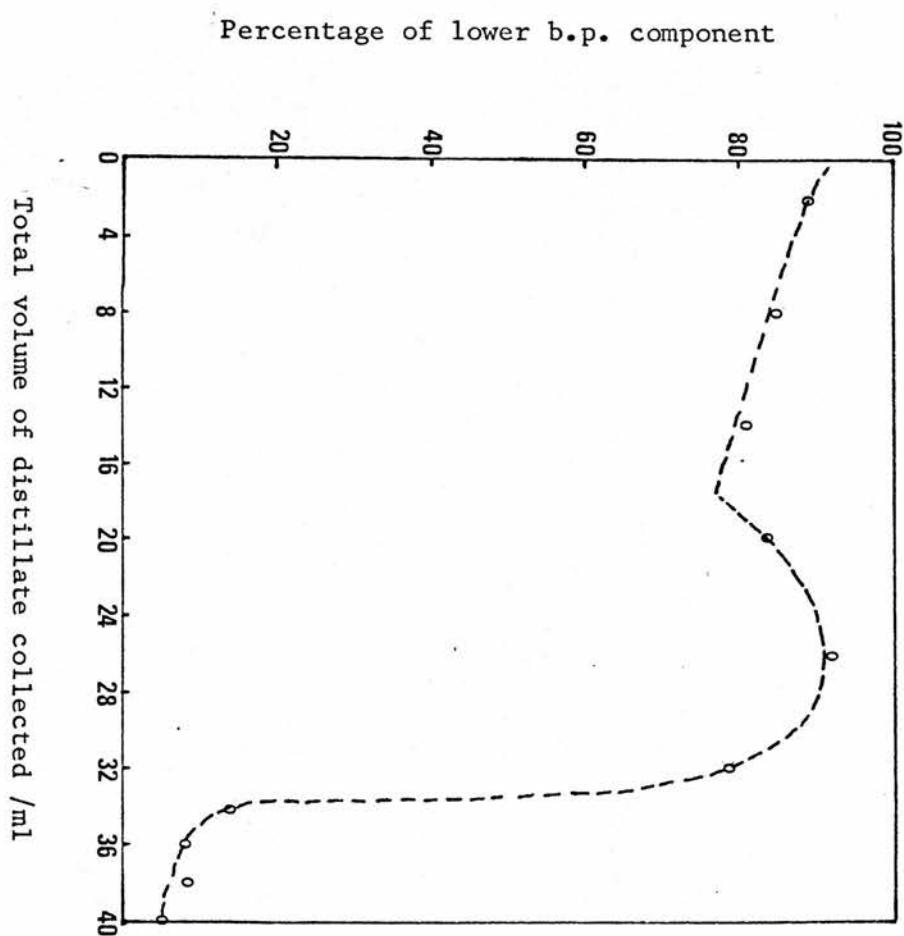


Figure 4 : Distillation of ethyl acetate, n-butyl acetate mixture using a Hélenistic still

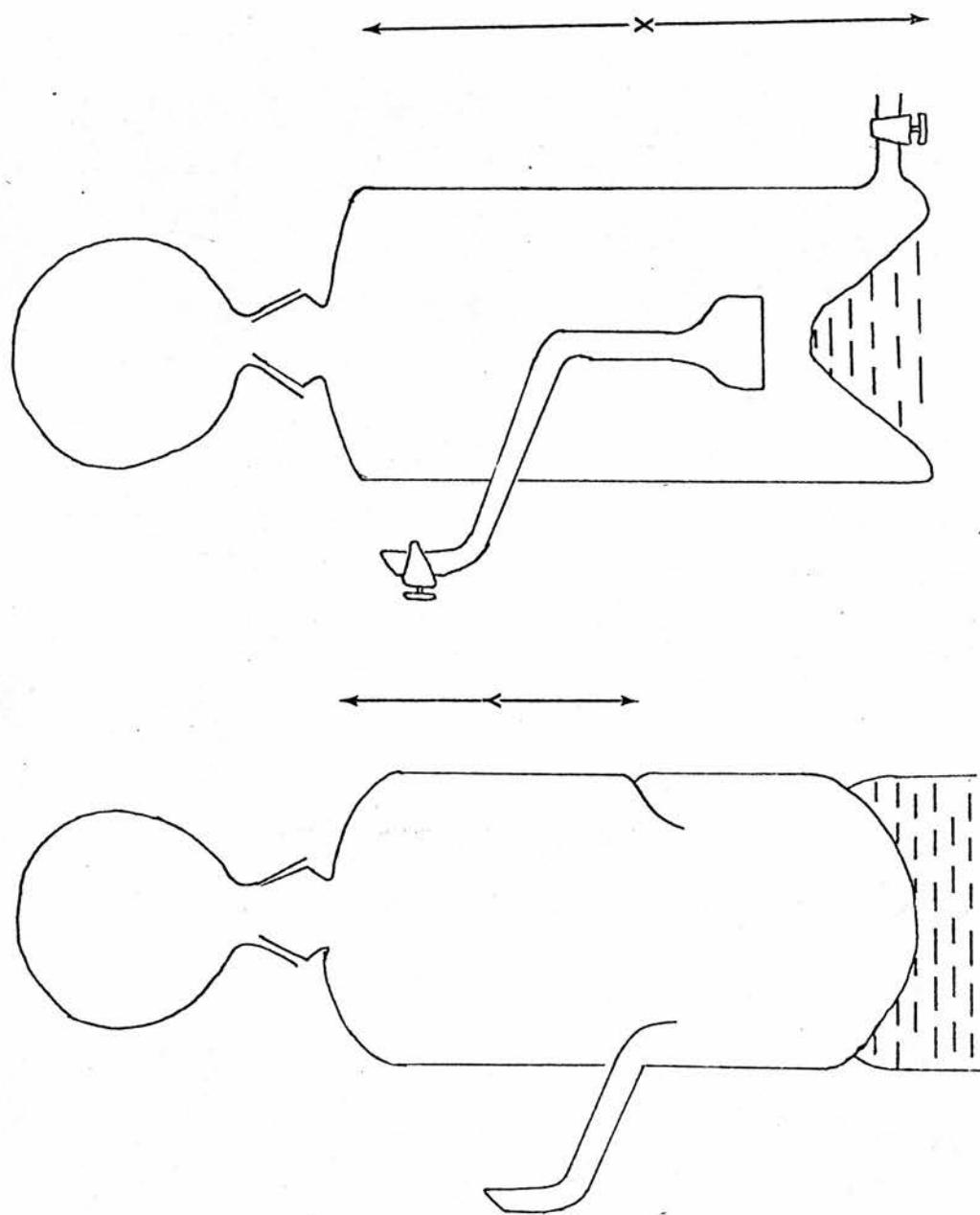
Table 1. Data from the distillation of ethyl acetate/n-butyl acetate mixture using the Hellenistic still.

Percentage of n-butyl acetate			Percentage of n-butyl acetate		
Sample No.	run 2	run 3	Sample No.	run 2	run 3
1	91.6	91.3	11	80.9	82.0
2	88.9	89.0	12	85.1	85.1
3	86.5	86.5	13	86.6	88.0
4	84.3	84.2	14	88.3	90.9
5	83.4	83.5	15	90.6	92.3
6	80.7	81.2	16	78.2	78.2
7	81.2	81.0	17	13.8	13.7
8	79.4	79.5	18	5.8	6.5
9	79.7	79.9	19	4.7	4.9
10	79.8	79.8	20	5.1	4.0

We can offer no satisfactory explanation but the matter will be commented upon later.

Second, the Hellenistic still is remarkably efficient in the separation of the two esters, but a careful comparison of the data in figure 3 and 4 shows that the Chinese still is slightly better. The effect is small but real. Repetition of the experiment consistently gave the same result. We can see why the Hellenistic still is less efficient by reference to figure 5. Vapour and liquid are in contact as the condensate runs down the outer walls of the vessel. The still becomes more efficient as this "time of contact" increases. In the Chinese still, contact occurs as the condensate descends the total height of the distillation vessel (ie x). In the Hellenistic still the annular collecting ring is some way below the top of the vessel and significant contact between vapour and liquid occurs only below the

Figure 5 : Glass models of (a) Chinese still and (b) Hellenistic still



rim (ie over height y). Above the rim, condensate enriched with n-butyl acetate does not fall back into the pot but is collected. It appears therefore, that the central catchbowl of the Chinese still does give rise to a better separation of the components of a liquid mixture. Both however, appear to be more efficient in separating the ester mixture, compared to a modern distillation apparatus with Liebig condenser. In figure 6 all three graphs are redrawn together for comparison. On the other hand, in terms of the rate of distillation, the modern and Hellenistic were very similar, but both were faster than the Chinese still.

Returning to the original question of which between the Chinese and Hellenistic stills is the more efficient, our results indicated that the Chinese still appeared to give the better separation. There is a simple manner in which we can test this hypothesis. Part of the condensing capacity of both Hellenistic and Chinese still is due to air cooling and this will occur more readily with liquids of high boiling points. The difference in the fractionating abilities of the two stills should be increased as the boiling points of the components in the liquid mixture are increased. The ability of an air-cooled surface to condense a vapour depends, of course, upon the difference in the temperature of the vapour and ambient temperature. The rate of heat loss is proportional to the temperature difference raised to a power, with radiant

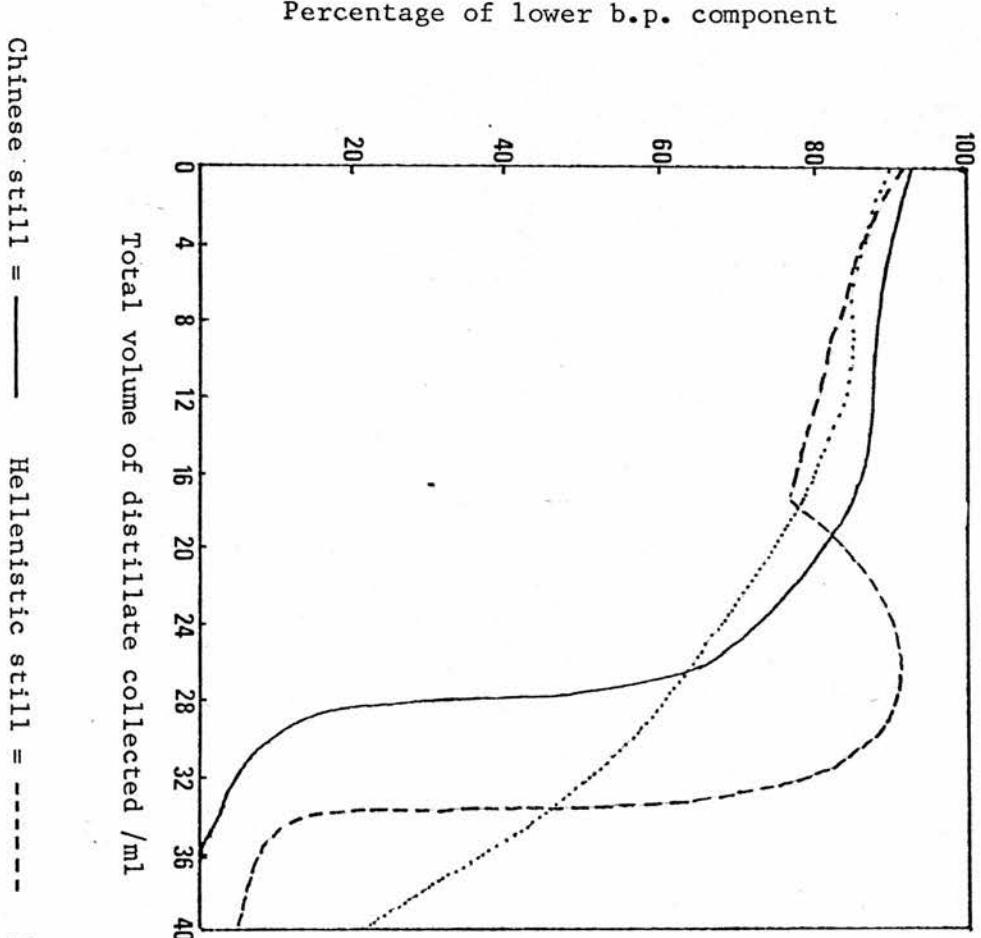


Figure 6 : The efficiency of the Chinese, Hellenistic and Modern stills

redrawn together for comparison

heat loss in a draught it is the fourth power (Stefan's law $U = \sigma T^4$ where U is total amount of energy per unit volume, σ is a constant, T is temperature.) With the imprecise conditions we used we cannot be specific, but we are certain that with a large temperature difference, condensation will occur very readily, but much less readily as the temperature difference decreases. This is easily demonstrated, as we have shown later.

First of all we turned to a binary mixture of two liquids which is regular and with higher boiling points. Thus we expect the degree of separation to be more apparent, proving a definite difference in the efficacy of the stills exists. The mixture chosen was anisole (bp 110°C) and toluene (bp 155°C). A 50:50 mixture of anisole and toluene was distilled in both the Chinese and Hellenistic stills under the same experimental conditions as before and the results are displayed in figure 7. Again analysis was carried out using a gas-liquid chromatograph as before. The flame ionisation detector has a wide linear range and a high sensitivity, however it does not respond fully to oxygenated hydrocarbons such as carbonyls. Thus the response of this detector is proportional to the number of carbon atoms, but diminishes with increasing substitution of an electron capturing species. The glass column (5 ft long, $\frac{1}{4}$ " diameter) contained 20% EGGS-X coated onto chromosorb (100-120 mesh). The EGGS-X column was used at an oven temperature of 65°C. The availability of this column dictated its use rather

than it being chosen specifically for the problem. The separation of these two components is relatively easy, due to the large difference in their respective vapour pressures. The standard calibrant used was a 50:50 (vol/vol) mixture of anisole/toluene. Quantitation of peak was based on the multiplication of peak height and retention time. By a simple application of proportion, the amount of each component in the sample mixture was reported as a volume percentage.

The response to the calibrant in terms of weight percent was not 50:50, due first, to the difference in density, anisole having the greater density and thus a larger amount of it would be injected, and secondly, the fact that anisole has an oxygenated carbon, which means that the detector does not fully respond to it. These together resulted in the standard peak area for anisole being 55.5% of the total volume, and for toluene 45.5%.

From figure 7, the improved performance of the Chinese over the Hellenistic still is more evident. At high temperatures, there is more effective partial reflux and hence fractionation, and the difference in the areas of the stills over which partial reflux can occur results in better separation with a Chinese still.

It should be noted that there is no peak in the concentration of the lower boiling fraction with the Hellenistic still. This phenomenon appears to be characteristic of the ester mixture.

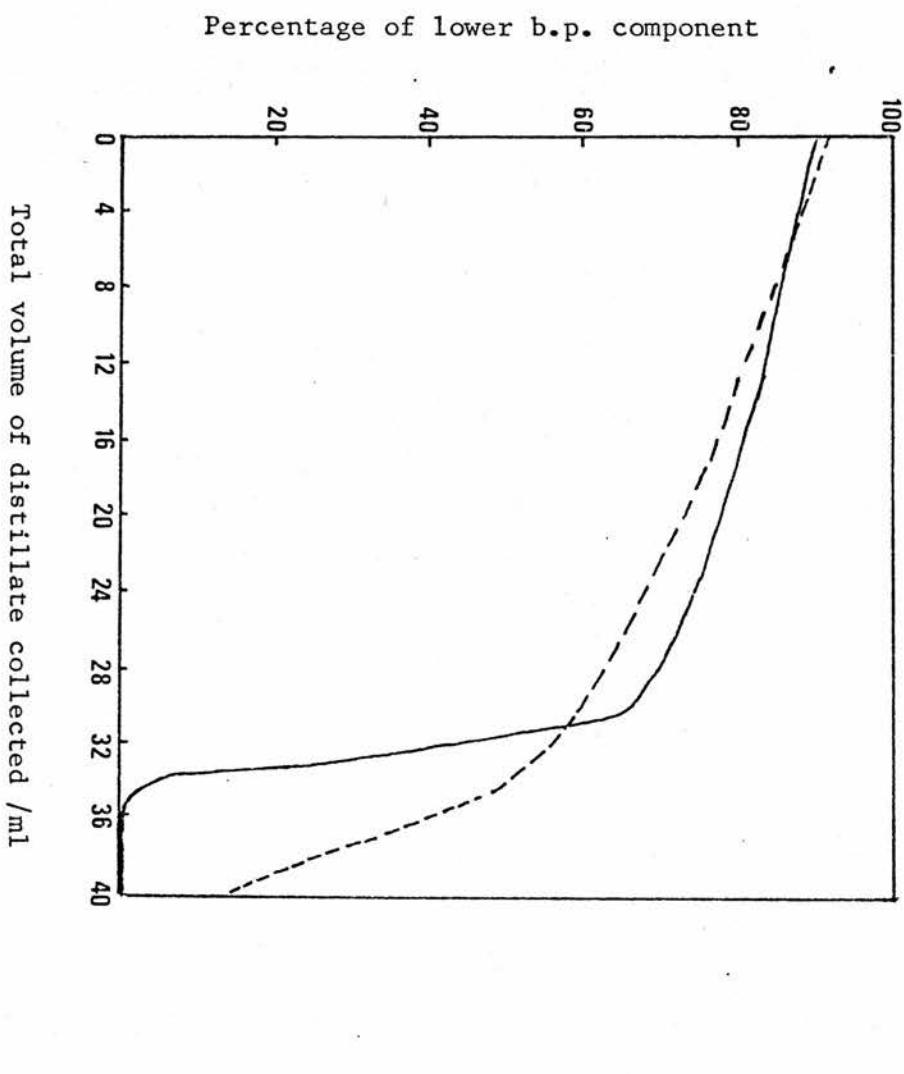


Figure 7 : Comparison of the distillation using a Chinese and a Hellenistic still of the toluene, anisole mixture

The temperature differences for the ester mixture and the anisole/toluene mixture was 49°C and 45°C respectively. If lower temperature mixtures with a smaller temperature difference are examined, in view of our previous reasoning, one would expect the difference between the efficacy of the stills to be less than has already been observed. Two other mixtures were examined; isopropyl acetate (bp 91°C) and isobutyl acetate (bp 117°C), $\Delta T = 26^\circ\text{C}$; ethyl isobutyrate (bp 110°C) and methyl isobutyrate (bp 93°C), $\Delta T = 17^\circ\text{C}$. Both of these mixtures were initially distilled using a modern distillation apparatus with a vigreux column, and this was used as a standard with which to compare the distillations carried out using the Chinese and Hellenistic stills. For separation of liquids with such close boiling points to be achieved, the use of the vigreux column was essential otherwise little if any effect would be obtained in a single distillation. All three distillations of both mixtures are represented in figures 8 and 9. A note is made here concerning the difference between the relative areas under the curves. The area under the Chinese still graph is small due to loss of sample through evaporation. This loss is the result of extended distillation time over other stills. With the isopropyl acetate/isobutyl acetate mixture, again the Chinese still appears to achieve a slightly better separation than either of the other two. The effect is not very dramatic however, and very much less obvious than any difference already observed, see figure 8. Any difference between the stills with

Percentage of lower b.p. component

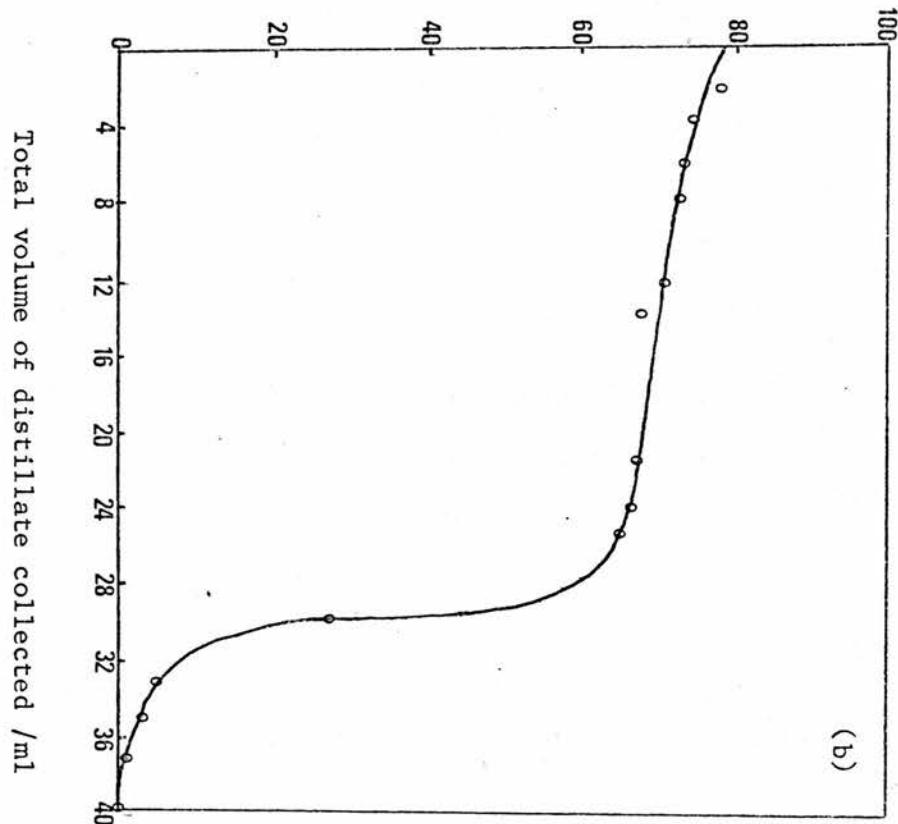
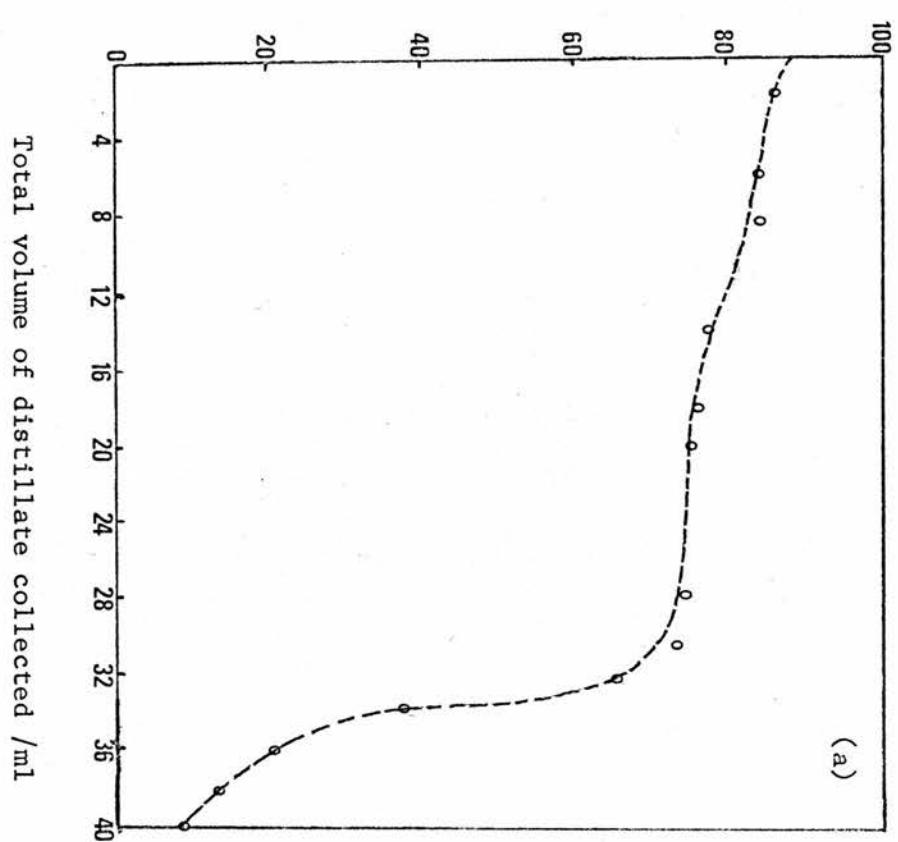


Figure 8 : Distillation of isopropyl acetate, isobutyl acetate mixture using (a) Hellenistic (b) Chinese still

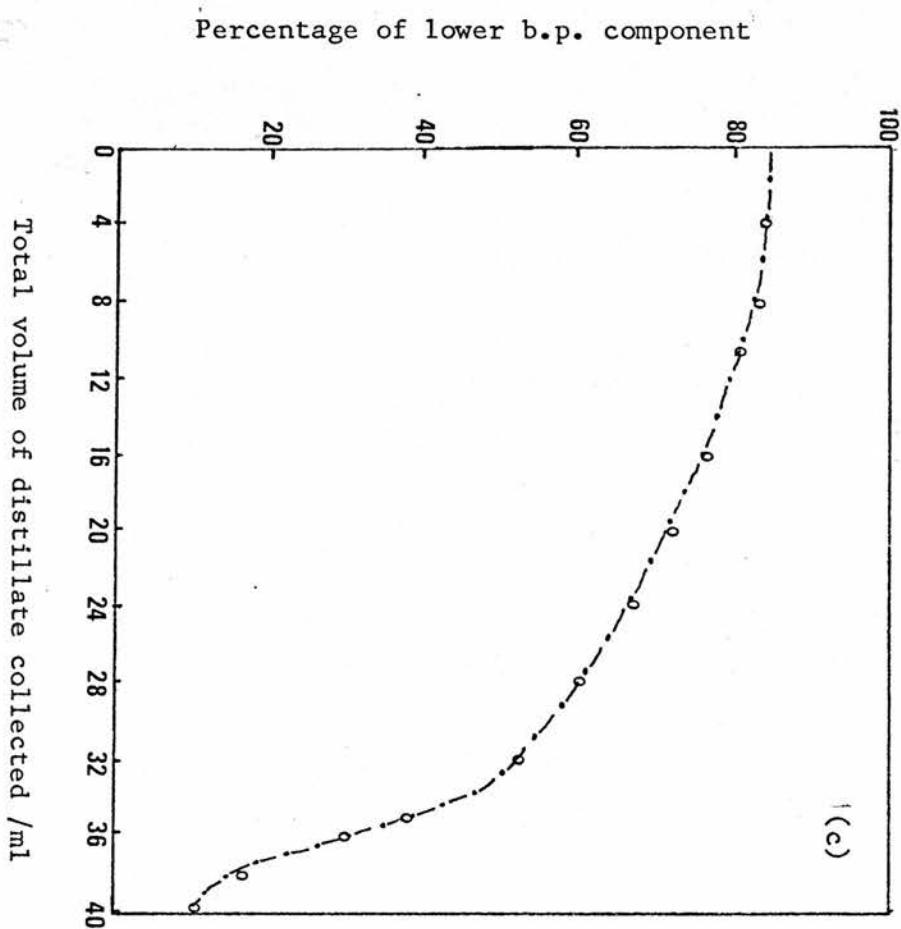


Figure 8 : Distillation of isopropyl acetate, isobutyl acetate mixture using (c) Modern still with Vigreux column

Percentage of lower b.p. component

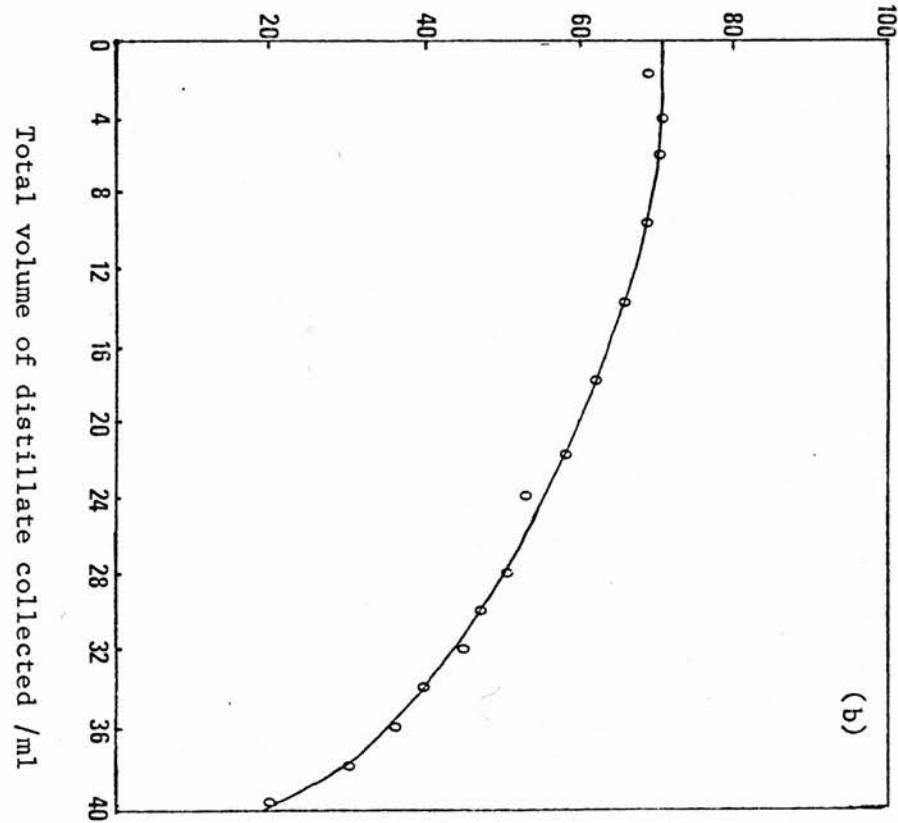
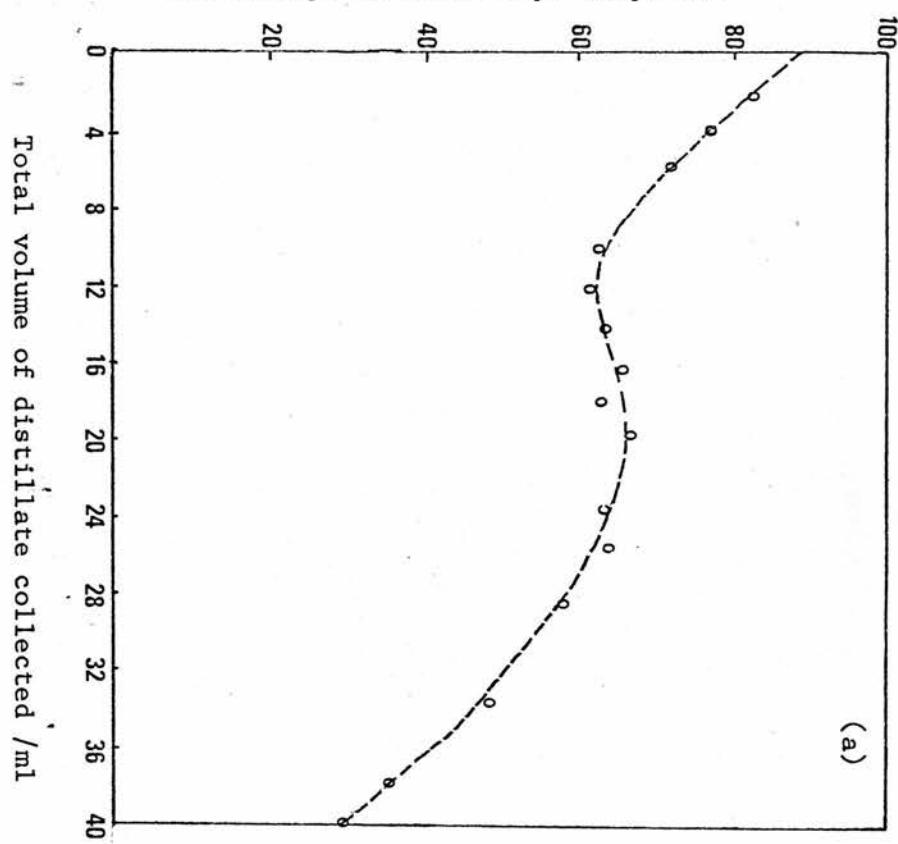


Figure 9 : Distillation of methyl isobutyrate, ethyl isobutyrate mixture using (a) Hellenistic (b) Chinese still

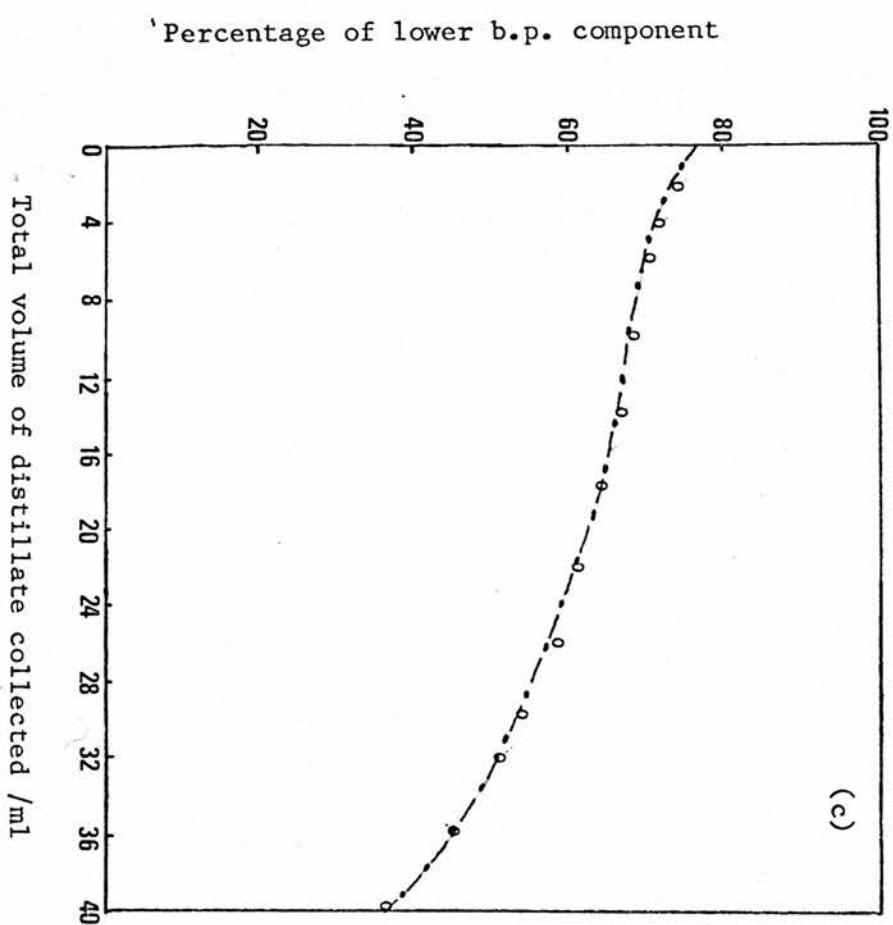


Figure 9 : Distillation of methyl isobutyrate, ethyl isobutyrate mixture using (c) Modern still with Vigreux column

the ethyl-isobutyrate/methyl isobutyrate mixture is barely discernible, if present at all, figure 9. No still achieves separation of components with boiling points as close as this and therefore all three stills are inefficient as distilling apparatuses.

So little is known of the distillation of essential oil in China, that the historical consequences of the ester experiment cannot be stated with certainty. What one would like to find is texts which describe the distillation of the higher boiling point essential oils, dating from 5th, 6th or 7th centuries A.D. ie before the appearance of strong alcohol in China. Then the distillation of essential oils would be regarded as a well-developed activity of this period, possibly arising from the excellence of the Chinese still. Such a find would throw a very different light on the question of where and by whom alcohol was first distilled.

One criticism of this work requires comment. The idealised glass stills, made in a modern workshop, used in this study, might be thought to bear little resemblance to the crude stills of the Chinese or the Hellenistic proto-chemists. However, the principles of vapourisation, condensation and reflux are so simple, that a few leaks or a wood fire as a source of heat, would make little difference. Our aim was to make comparisons, although far from the minds of early European or Chinese distillers, which necessitated careful construction of the stills. On the other hand, our model Hellenistic still,

resembles in principle, but not in shape, the alembic of the Alexandrian proto-chemists. Their stills had a smaller surface area for reflux. Consequently the difference found with our models may well be less than that which would be obtained with authentic stills.

CHAPTER 2

Thoughts on the Smelting of Aluminium in Medieval China

The acquisition of chemical and technological knowledge concerning objects and materials from antiquity is in itself of value. Such knowledge can provide information on the stage of advancement of technological processes of a culture during a particular era. In addition, the chemical investigation of ancient materials may occasionally contribute to chemical knowledge itself, as well as to archaeology.

In the light of the great successes achieved in science and technology by the medieval Chinese, one can see why the discovery of aluminium ornaments during an excavation of a tomb in Eastern China was taken very seriously by both East and West alike. The excavation in 1956 was undertaken at Yi-xing, in Jiang-su Province in Eastern China, which according to tradition is said to be the tomb of a famous general of the Jin era (265-420 A.D.), Zhou Chu, who died in 297 A.D. There a number of metal belt ornaments in quite good state of preservation was uncovered, by one of China's leading archaeologists, Lou Zong-chen. A detailed report of the excavation was published in a long article by Lou Zong-chen.¹² The belt ornaments were found by the waist of the body and from the position on the ground should be the buckle of the dead man's belt. They comprised over twenty pieces, some were more or less complete others were fragments and were of different shapes. These pieces were said to have been 'covered with the corrosion and earth of more than a thousand years'. The outer

surface of some of the pieces was grey-brown, the inner layer was white and had a metallic sheen. Since this find aroused attention among archaeologists a piece was selected and sent to Nanjing University Chemistry Department for chemical analysis to be carried out. The findings as a result of chemical analysis reported the composition of the alloy in the inner part of the belt ornament to be 85% aluminium, 10% copper and 5% manganese.

Following this an article was published,¹³ which suggested that Chinese craftsmen of the Jin Dynasty were able to make an alloy of copper and aluminium. Although the whole excavation was of historical importance, it was the supposed discovery of ornaments made of aluminium alloy which attracted most attention and news of it quickly spread appearing in as many as five different languages, initially in Chinese, then Russian, Swedish, French and finally, English.

By 1000 B.C. China had already entered the Bronze age. Besides accumulating rich experience in smelting and casting, the age must have mastered the technique of high temperature above 1000°C without which copper cannot be fused. By the Warring States period (480-221 B.C.), the Chinese began to use cast iron, therefore the temperature of 1200°C must have been attained. During the 400 years of the Han Dynasty (202 B.C. - 221 A.D.), arising out of the needs of production and technical improvement, the techniques of iron smelting and of obtaining high temperatures were continuously improved.

The use of nickel alloys in medieval China was yet another achievement. In the last years of the Eastern Han Dynasty (25-221 A.D.), Tu Shi, summarising the experience of the labouring people created the hydraulic blower. This was a still more important key to further technological advances, as powerful blowing equipment is essential for obtaining high temperature. There was another significant advance, that is the use of coal as a fuel. Daoism flourished from Wei and Jin times onwards (220-265 A.D.) with more and more people practising it. They were concerned with two things in particular, the extraction of the 'golden elixir' of immortality and the forging of a magic sword, both of which are connected with the smelting of metals. They constantly mixed metals and minerals together and heated them, sometimes adding other substances. Therefore it is quite possible that in the course of long periods of time they may have inadvertently discovered a new substance or stumbled on some new techniques. A practitioner of the Daoist arts discovered the method of smelting steel and made the earliest steel sword in the world.

On reflection of the social conditions of the period, in particular the stage of advancement of Chinese metal technology, the idea that an aluminium-copper alloy was also made during that time is not beyond the realms of possibility.

During the Jin and North-South periods, there were outstanding achievements in other sciences and disciplines in China, the calculation of pi, the knowledge of the preparations

of elixirs, advances in pharmacy contained in the Chi Min Yao Shu to name but a few, all of which were epoch making scientific creations. Thus any special achievements in metallurgical chemistry would fit in with the high level developments in other branches of the natural sciences.

To avoid any possible mistake in the chemical analysis of the belt buckle, another sample piece was submitted to chemical tests and qualitative spectroscopic analysis by Yang Gen¹⁴ of the Department of Engineering Chemistry Tsinghua University who confirmed the presence of a large proportion of aluminium. Attention should be drawn to the fact that, in general, qualitative and quantitative spectroscopic analyses are usually applied to the detection and estimation of minute amounts or traces of substances. The accuracy of such analysis is seldom greater than $\pm 5\%$ of the amount of substance present, and, as a rule, this represents a rather large error compared with the accuracy of chemical methods, except when the amount of substance or element present is very small. The investigation did not stop there. Further examinations were carried out, and as a result of these, some doubt was thrown on the matter. Chemical tests on separate pieces, showed the alloy to be silver-based and not aluminium-based. Addition of hydrochloric acid to the dissolved material resulted in a white precipitate of silver chloride. On addition of an excess of ammonia, this re-dissolved and a pale coloured solution containing $[\text{Cu}(\text{NH}_3)_2]^{2+}$ resulted, indicating the presence of

copper. Absence of a precipitate at this stage showed the concentration of aluminium in it was extremely minute. Spectroscopic examination, X-ray diffraction and electron microscope investigation, confirmed these findings. These pieces of silver-belt ornaments were identified as the type prevailing during the third and fourth centuries in China. These were usually of silver-bronze or gilt bronze and are illustrated in photograph 1.

To summarise, the results collectively showed that four of the pieces examined were silver-based alloys with traces of aluminium and three pieces examined were aluminium. Doubt was cast on the discovery and a controversy arose regarding it. The authenticity of the aluminium buckles was questioned by a number of Chinese archaeologists including Xia Nai.¹⁵ Was the isolation of aluminium possible, bearing in mind the temperature the Chinese could have attained? If the aluminium pieces are authentic, was their occurrence accidental or was it obtained intentionally? What possible technique could the early Chinese people have used?

To obtain aluminium from its ore is rather difficult because of most of the ore remains as the oxide. This is because aluminium oxide has a very low dissociation pressure and so it is difficult to reduce. Further, under high pressure, when the oxide is reduced with charcoal, aluminium vapour easily reacts with the charcoal, forming the carbide analogous to pig iron, so that metallic aluminium is not

obtained.

The history of the isolation of aluminium is well documented. The chemical isolation of metallic aluminium preceded by many years its electrolytic preparation. Pure aluminium was first isolated in the West in 1824 when Wöhler¹⁶ obtained the metal as a grey powder by the action of potassium on aluminium chloride and in 1854 Deville¹⁷ obtained the metal by reaction of the chloride with sodium. Later Héroult isolated the metal by electrolysis.

Ruprecht and Tondi¹⁸ claimed to have obtained aluminium from its oxide by heating alumina with charcoal dust covered with a layer of bone-ash in a fireclay crucible. Silliman¹⁹ fused alumina on a charcoal block by means of an oxy-hydrogen flame and noted small metallic globules which burned brightly. Berzelius told Davy in a letter that he had reduced alumina²⁰ by heating with carbon and iron but, since no reference is made to this in Berzelius' later writings, it is assumed he must have made a mistake. In 1825 Oersted prepared aluminium chloride by passing chlorine over a mixture of aluminium oxide and charcoal while heating to redness. Subsequent reaction with potassium amalgam and removal of the mercury in the absence of air gave a lump of metal rather like tin which may have been impure aluminium.²¹ However publication in an obscure Danish journal meant the paper was not widely read. Wöhler was unable to repeat the preparative procedure. He prepared aluminium chloride in the same manner but converted it to the element by

reaction of potassium alone as previously stated.¹⁶ The grey powder obtained was not pure and it was not until 1845 that Wöhler was able to melt this to a coherent mass. It seems very probable that preparation of the anhydrous chloride involved reduction of the oxide to the metal by charcoal and immediate reaction to give the volatile chloride. It is possible to reduce aluminium oxide to the metal by heating with charcoal, and the production of iron and steel by this process was well established in China, by the Jin Dynasty. This process is never used today for the production of aluminium, because of the very high temperature required, even if there were no other objections.

How could the Jin Dynasty people master a comparatively difficult technique and obtain an aluminium-copper alloy. A process was described by Cowles et al,²² whereby alloys containing aluminium were produced by the carbon reduction of the oxide in the presence of the alloying metal. This was significant in that the initial report¹⁴ stated that the belt ornaments were made of an alloy containing 85% aluminium, 10% copper and 5% manganese. Although the process described by Cowles et al²² employs an electric current, it is solely for the purpose of heating the reaction mixture. The temperature attained was not recorded. There is no reason why reduction of oxide should not occur when the mixture is heated to the same temperature by another method. These authors report that 'when the reduction of aluminium is conducted in the absence of other metals it forms a carbide as it comes from the blast furnace'.

However, the addition of a second metal to the reaction mixture resulted in the formation of alloys which were ready for casting, with no interference from the carbon present.

Aluminium-copper and aluminium-iron alloys were obtained in this manner. Thus, if there is sufficient quantity of any metal with a boiling point greater than aluminium (eg copper bp 2300°C) present in the reaction, the aluminium as soon as it is reduced, will be dissolved in that metal to form an alloy with no interference from the carbon present. Since the liquid alloy contains aluminium, its vapour pressure must be lower than that of the pure aluminium, a fact favourable to the reaction process. At the same time the partial pressure of carbon monoxide must be lower than the atmospheric pressure. Thus, the temperature, as the reaction proceeds, may be lower than 2000°C. The process was never exploited commercially since in 1886 the superior cryolite²³ method, which is used to this day, was devised. This method, which uses electricity, was obviously impossible in Jin dynasty China. The small amount of experimental evidence to hand makes the smelting of aluminium in Jin dynasty China very surprising, but not out of the question. Carbon reduction may have been a way in which the Chinese obtained their aluminium-copper alloy.

Other ways of obtaining such alloys have been proposed but can be disregarded, e.g the production of sodium by charcoal at high temperature, or by reducing sodium chloride with lead. Sodium could take the place of successive amounts

of aluminium in the mineral substance and the aluminium would then immediately dissolve in the molten copper. These ideas are difficult to believe, because it is not easy to obtain sodium from either the reduction of sodium chloride by lead or the reaction between charcoal and caustic soda, particularly when the extent required for reduction is considered. In such a system, by the time the sodium has entered the vapour state (bp 880°C) the reduction reaction has not yet reached the rate required for it to proceed (m.p. of aluminium oxide is 2050°C), so the likelihood that these two reactions proceed together is not great.

With the passage of time the authenticity of the aluminium alloy buckles was discussed by a number of Chinese archaeologists. However, it proved too early to draw conclusions on the basis of both the chemical and archaeological evidence, not only due to the divergences in identification, but because many basic questions had not been answered. Therefore when we became involved we felt the archaeological evidence left the matter undecided and for this reason undertook an investigation.

Taking a fresh approach, we set out to examine the feasibility of aluminium smelting with the technology available in Jin dynasty China. This we did, not by further experimentation, but by thermodynamic calculation. It is known that if a metal is alloyed as it is smelted, the temperature at which reduction occurs is lowered. We thought it would be of

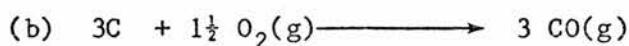
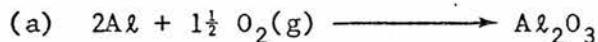
value to calculate the temperature of reduction of aluminium oxide in the presence of other metals, in order to see at what temperature an alloy containing 85% aluminium could be produced. Such calculations make a number of assumptions and are therefore subject to uncertainty, but they should give more information towards the feasibility of aluminium smelting in Jin dynasty China.

The temperature of reduction of aluminium oxide, as a pure metal and as alloys has been calculated. This is best achieved by a study of free energy-temperature, or Ellingham diagrams after Ellingham²⁴ who constructed the original diagrams. These are plots of the standard free energy of formation of oxides (or sulphides, etc) against temperature. Thermochemical data are taken from the compilation of Kubaschewski et al.²⁵.

The overall stoichiometry of the reaction is:-



To calculate the temperature at which reduction of aluminium occurs, we take the above and transform it into two half equations;



The free energy change for each half equation is calculated from the expression

$$\Delta G_T^\theta = \Delta H_{298}^\theta + \int_{298}^T \Delta C_p^\theta dT - T \Delta S_{298}^\theta - T \int_{298}^T \Delta C_p^\theta / T dT \quad (i)$$

Values of H_{298}^θ and S_{298}^θ for all reactants are known. For each half reaction;

$$\Delta H_{298}^\theta = \sum H_{\text{products}}^\theta - \sum H_{\text{reactants}}^\theta$$

$$\Delta S_{298}^\theta = \sum S_{\text{products}}^\theta - \sum S_{\text{reactants}}^\theta$$

The calculation of ΔC_p^θ is slightly more complex. The general expression for C_p as a function of temperature is:

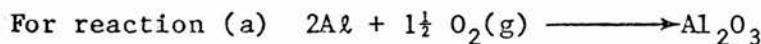
$$C_p = a + bT + cT^{-2}$$

The choice of formulae here depends on the temperature range in which the slope of the curve varies most.

$$\Delta C_p^\theta \text{ is calculated using } \Delta C_p_{298}^\theta = \sum C_p_{\text{products}}^\theta - \sum C_p_{\text{reactants}}^\theta$$

Values of a , b and c for Al, O₂, Al₂O₃, C and CO are all known.

Calculation of ΔG_T^θ for each half equation is now possible.



$$\Delta H_{298}^\theta = -400\,000 \text{ cals}$$

$$\Delta S_{298}^{\theta} = -74.84 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$\Delta C_p^{\theta} = 4.86 - 3.17 \times 10^{-3} T - 6.22 \times 10^5 T^{-2}$$

This latter expression is integrated to give:

$$\int \Delta C_p^{\theta} dT = 4.86T - 1.585 \times 10^{-3} T^2 + 6.22 \times 10^5 T^{-1} + k_1 \text{ where } T = 298\text{K}$$

$$\int \Delta C_p^{\theta} dT = 3394.78 + k_1$$

$$\therefore k_1 = -3394.78$$

$$\text{Therefore, } \int_{298}^T \Delta C_p^{\theta} dT = 4.86T - 1.585 \times 10^{-3} T^2 + 6.22 \times 10^5 T^{-1} - 33.94.78$$

The ΔC_p^{θ} expression, divided by temperature and integrated in the same manner, gives

$$\int_{298}^T \Delta C_p^{\theta}/T dT = 4.86 \ln T - 3.17 \times 10^{-3} T + 3.11 \times 10^5 T^{-2} - 30.25$$

Substitution of the appropriate terms in the expression for ΔG^{θ} gives:

$$\begin{aligned} \Delta G_T^{\theta} &= -403394.78 - 11.193T \log T + 1.62 \times 10^{-3} T^2 \\ &\quad + 3.11 \times 10^5 T^{-1} + 109.95T \end{aligned} \tag{ii}$$

From this equation, ΔG^{θ} values for the equation (a) can be calculated at different temperatures. It should be noted that the heat c values used are only valid in the range 298 to 932 K. This energy formula (i) is thus only applicable to

temperatures up to 932 K. To evaluate the free energy of formation above this temperature range, the free energy of melting of aluminium must be introduced. The heat of this reaction is double the heat of fusion of aluminium but opposite in sign

$$\Delta H_{932}^{\theta} = -2 \times 2500 = -5000 \text{ cal}$$

$$\Delta S_{932}^{\theta} = -5000/932 = -5.35 \text{ cal K}^{-1}$$

$$\Delta C_p^{\theta} = -4.12 + 5.92 \times 10^{-3}T$$

$$\int_{932}^T \Delta C_p^{\theta} dT = -4.12T + 2.96 \times 10^{-3}T^2 + 1269$$

$$\int_{932}^T \Delta C_p^{\theta}/T dT = -9.49 \log T + 5.92 \times 10^{-3}T + 22.66$$

Substitution of these terms in the expression for ΔG^{θ} gives:

$$\Delta G_T^{\theta} = -3731 + 9.49T \log T - 2.96 \times 10^{-3}T^2 - 21.43T \quad (\text{iii})$$

This is the equation for the change of free energy of melting of two moles of aluminium. As with all equilibrium phase changes, at the melting point it is zero, but it has a finite value which is additive in computing free energies above the melting point from values which are valid below this temperature. Thus to find ΔG_T^{θ} for temperatures between 932 and

1273 K, the free energy expressions (ii) and (iii) are added to give expression (iv)

$$\Delta G_T^\theta = -408\ 208 - 6.19T \log T - 0.78 \times 10^{-3} T^2 + 3.93 \times 10^5 T^{-1} + 102.19T \quad (iv)$$

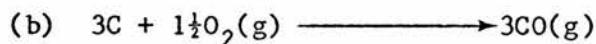
The errors in formulae such as these vary within rather wide limits, due mainly to the error in the experimentally determined values of the heats of formation at room temperature. Errors may range from 3 000 to 5 000 cal. One consequence of this is the figures for these free energy expressions may be rounded off without loss of accuracy. Another is that in most cases virtually no loss in accuracy is involved by drawing the $\Delta G/T$ curves corresponding to an equation such as (i).

Using the equations found, the ΔG^θ for the half equation (a), at different temperatures, was calculated.

Table 1Thermochemical data for reaction (a)

Temp/K	$-\Delta G_T^\theta/\text{kcal mol}^{-1}$	Temp/K	$-\Delta G_T^\theta/\text{kcal mol}^{-1}$
0	404	1400	291
200	385	1600	274
400	370	1800	258
600	355	2000	242
800	340	2200	225
1000	323	2400	209
1200	307	2600	192

The same procedure was followed for the half equation (b)



$$\Delta H_{298}^\theta = -79200 \text{ cal}$$

$$\Delta S_{298}^\theta = 64.32 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$\int_{298}^T \Delta C_p^\theta dT = 2.67 - 0.81 \times 10^{-3} T^2 - 6.5 \times 10^5 T^{-1} + 3072.29$$

$$\int \Delta C_p^\theta / T dT = -2.67 \ln T - 1.62 \times 10^{-3} T - 3.285 \times 10^5 T^{-2} + 19.39$$

Substitution for these terms in the expression for ΔG_T^θ (i)
 gives equation (v)

$$\Delta G_T^\theta = -76.130 + 6.149T \log T + 0.81 \times 10^{-3}T^2$$

$$-3,275 \times 10^5 T^{-1} - 83.71T \quad (v)$$

Table 2Thermochemical data for reaction (b)

Temp/K	$-\Delta G_T^\theta/\text{kcal mol}^{-1}$	Temp/K	$-\Delta G_T^\theta/\text{kcal mol}^{-1}$
0	76	1400	166
200	92	1600	179
400	104	1800	191
600	116	2000	203
800	129	2200	215
1000	142	2400	227
1200	154	2600	239

Free energy formulae derived from application of equations of the type (ii) and (v) have often been given in the literature.²⁶

It should be mentioned that the formulae give an impression of a degree of accuracy which they do not possess. For appropriate calculations, simplified formulae may be used satisfactorily, such as;

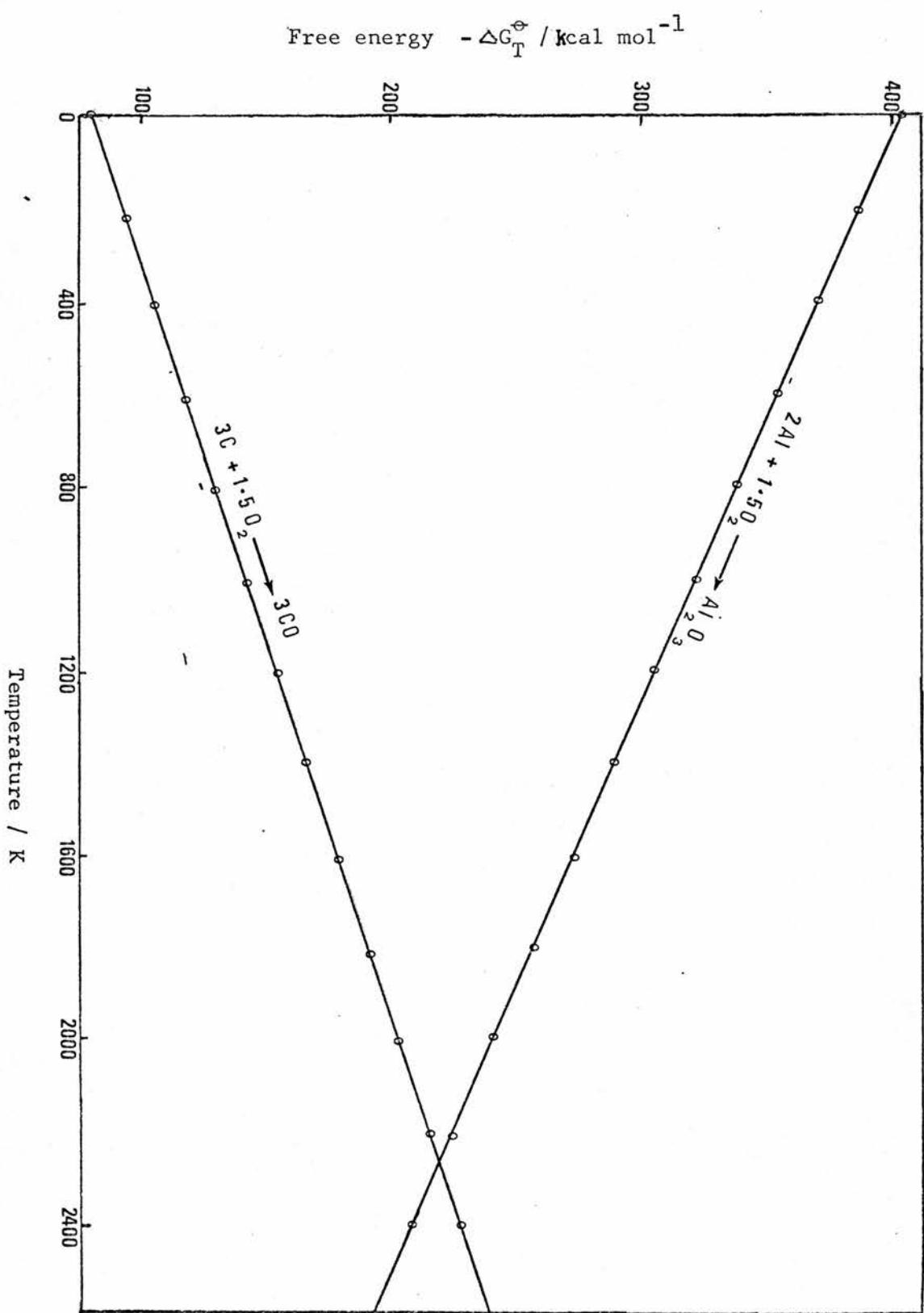
$$\Delta G^\circ = A + BT \log T + CT \quad (vi)$$

If ΔC_p° is very small, one could easily express the free energy relationship by a linear relationship. Instead of using room temperature values ΔH_{298}^θ and ΔS_{298}^θ , average values ΔH_x and ΔS_x should be derived from the temperature range in consideration. This method has been applied before²⁷.

A plot of ΔG_T^θ versus temperature for the two half reactions is shown in figure 1. At the point of intersection ΔG^θ for the reaction $2\text{Al} + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{Al}_2\text{O}_3$ (ΔG_a^θ) equals ΔG^θ for the reaction $3\text{C} + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow 3\text{CO}(\text{g})$ (ΔG_b^θ). Above the temperature of the point of intersection $\Delta G_a^\theta > \Delta G_b^\theta$ and so ΔG^θ for the overall reaction $\text{Al}_2\text{O}_3 + 3\text{C} \longrightarrow 2\text{Al} + 3\text{CO}(\text{g})$ (ΔG_c^θ) will be negative. At all temperatures when ΔG_c^θ is negative, the reduction of Al_2O_3 occurs spontaneously. The value obtained from figure 1 is 2280 K i.e 2007°C and this is the lowest temperature at which the reduction of Al_2O_3 by carbon can occur under equilibrium conditions.

It is impossible that this temperature could have been attained by the Chinese of the Jin dynasty. Even with modern technology, the construction of a furnace for work over 2000°C is both difficult and costly. What is amazing is that Cowles et al achieved it in, what appears to be, a rather casual manner. The method they used is hazardous as they had no way of controlling the resistance of the material in the furnace.

Following this, the effect of the presence of another metal, to form an alloy, upon the free energy of reaction was considered. For the two binary metallic systems $\langle\text{Ag-Al}\rangle$ and $\langle\text{Cu-Al}\rangle$, the difference in the free energy due to the presence of the other metal can be calculated. What is formed is the solution of one metal in another and such a solution system has been shown within the limits of experimental error, to exhibit regularity.



(1) The binary system silver-aluminium

The integral entropies of mixing for this system may be calculated from the following expression:

$$\Delta S_{\text{mix}}^{\theta} = -4.574 (x_1 \log x_1 + x_2 \log x_2)$$

By the use of this expression and the values given for $\Delta H_{\text{mix}}^{\theta}$, it is possible to calculate the values of $\Delta G_{\text{mix}}^{\theta}$, for mole fractions $x_2 = 0.1$ to 0.9 , where x_2 is the mole fraction of aluminium. To make the results comparable to the calculations for pure aluminium, the data have been corrected for the presence of two moles of aluminium. Using the equation $\Delta G_{\text{mix}}^{\theta} = \Delta H_{\text{mix}}^{\theta} - T\Delta S_{\text{mix}}^{\theta}$ and the thermochemical data from table 3, values of $\Delta G_{\text{mix}}^{\theta}$, the free energy difference between pure aluminium and aluminium in the alloy have been calculated. These, which are listed as a function of temperature and mole fraction of aluminium in table 4, are used to correct the $-\Delta G_T^{\theta}$ values of the pure metal (page 48)

Table 3Thermochemical data for Ag-Al alloy

mole fraction Al	$\Delta S_{\text{min}}^{\theta}/\text{cal K}^{-1}(2 \text{ mol})^{-1}$	$\Delta H_{\text{mix}}^{\theta}/\text{cal}(2 \text{ mol})^{-1}$
0.1	12.915	-13 600
0.2	9.940	-12 900
0.3	8.090	-10 333
0.4	6.685	-6 300
0.5	5.508	-3 240
0.6	4.456	-1 266
0.7	3.467	-114
0.8	2.485	+375
0.9	1.435	+378

Table 4Values of $-\Delta G_{\text{mix}}^{\theta}$ in kcal mol $^{-1}$ as a function of x_2 and temperature

Temp/K	$x_2 = 0.1$	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	13.6	12.9	10.3	6.3	3.2	1.3	0.14	-0.38	-0.38
200	16.2	14.9	12.0	7.6	4.3	2.2	0.84	0.12	0.09
400	18.8	16.9	13.6	9.0	5.4	3.0	1.53	0.62	0.20
600	21.3	18.9	15.2	10.3	6.5	3.9	2.2	1.12	0.48
800	23.9	20.9	16.8	11.6	7.6	4.8	2.9	1.61	0.77
1000	26.5	22.8	18.4	13.0	8.7	5.7	3.6	2.11	1.06
1200	29.1	24.8	20.0	14.3	9.8	6.6	4.3	2.61	1.34
1400	31.7	26.8	21.7	15.7	11.0	7.5	5.0	3.10	1.63
1600	34.3	28.8	23.3	17.0	12.1	8.4	5.7	3.60	1.92
1800	36.8	30.8	24.9	18.3	13.2	9.3	6.4	4.10	2.21
2000	39.4	32.8	26.5	19.7	14.3	10.2	7.1	4.60	2.49
2200	42.0	34.8	28.1	21.0	15.4	11.1	7.8	5.09	2.78
2400	44.6	36.8	29.7	22.3	16.5	12.0	8.5	5.59	3.07
2600	47.2	38.7	31.4	23.7	17.6	12.9	9.2	6.09	3.35

Table 5 shows the free energy change for the reduction of aluminium in the presence of silver.

Table 5

Values of $-\Delta G_T^\theta$ in kcal mol⁻¹ as a function of x_2 and temperature

Temp/K	$x_2 = 0.1$	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	390	391	394	398	401	403	404	404	404
200	369	370	373	377	381	383	384	385	385
400	351	353	356	361	365	367	369	369	370
600	334	336	340	345	349	351	353	354	355
800	316	319	323	328	332	335	337	338	339
1000	297	300	305	310	314	317	319	321	322
1200	278	282	287	293	297	300	303	304	306
1400	254	264	269	275	280	284	286	288	289
1600	240	245	251	257	262	266	268	270	272
1800	221	227	233	240	245	249	252	254	256
2000	203	209	216	222	228	232	235	237	240
2200	183	190	197	204	210	214	217	220	222
2400	164	172	179	187	193	197	201	203	206
2600	145	153	161	168	174	179	183	186	187

The values of ΔG_T^θ , for each x_2 , were then plotted against temperature and the points of intersection with the data for the half reaction (b) measured (Figure 2). These figures give the minimum temperature of reduction of aluminium oxide by charcoal in the presence of silver. They are listed in table 6.

Table 6

Minimum temperature of reduction Al_2O_3 in the presence of silver

x_2	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Temp/K	2000	2040	2080	2125	2170	2200	2225	2235	2260	2280

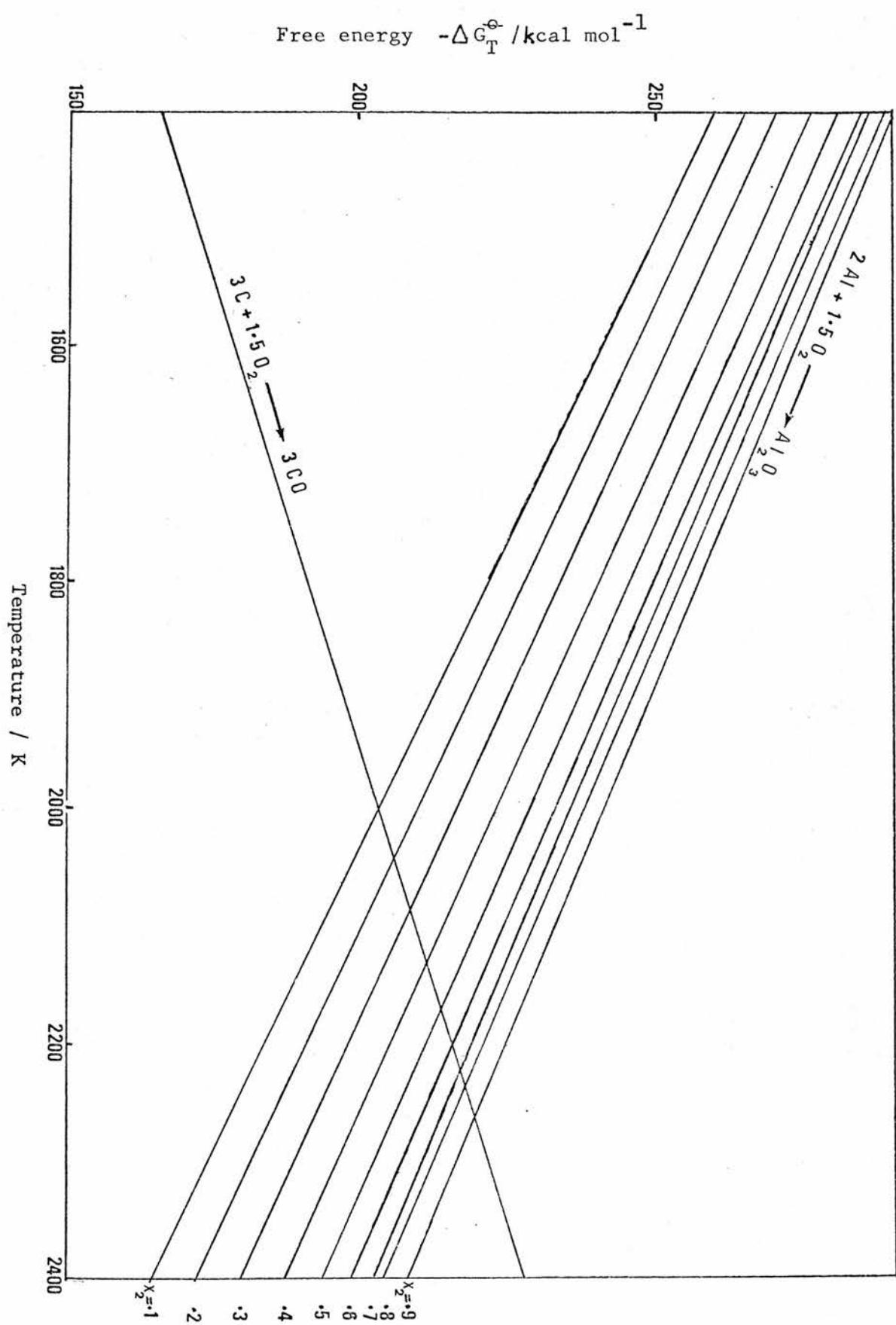


Figure 2 : Reduction of Al_2O_3 in the presence of Ag (X_2 = mole fraction of Al)

x_2 is the mole fraction of aluminium in the resulting alloy.

When $x_2 = 0.1$ the alloy contains only 2.7% aluminium, but, even at this low concentration, the smelting temperature is above that achieved in a simple furnace.

(2) The binary system copper-aluminium

The same calculations were applied to the reduction of Al_2O_3 in the presence of copper.

Table 7

Thermochemical data for Cu-Al system

mole fraction Al(x_2)	$\Delta S_{\text{mix}}^{\theta} / \text{cal K}^{-1} (2 \text{ mol})^{-1}$	$\Delta H_{\text{mix}}^{\theta} / \text{cal} (2 \text{ mol})^{-1}$
0.1	12.915	-32 000
0.2	9.940	-31 500
0.3	8.090	-28 667
0.4	6.685	-23 750
0.5	5.508	-17 000
0.6	4.456	-11 667
0.7	3.467	-7 714
0.8	2.485	-4 375
0.9	1.435	-1 999

These data are used to calculate $\Delta G_{\text{mix}}^{\theta}$ values which are listed as a function of temperature and mole fraction in table 8. These are then used to correct the $-\Delta G_T^{\theta}$ values of the pure metal.

Therefore table 9 shows the free change for the reduction of aluminium in the presence of copper.

Table 8

Values of $-\Delta G_{\text{mix}}^{\theta}$ in kcal mol⁻¹ as a function of x_2 and temperature

Temp/K	$x_2 = 0.1$	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	32.0	31.5	28.7	23.8	17.0	11.7	7.7	4.4	2.0
200	34.6	33.5	30.3	25.1	18.1	12.6	8.4	4.9	2.3
400	37.2	35.5	31.9	26.4	19.2	13.4	9.1	5.4	2.6
600	39.7	37.5	33.5	27.8	20.3	14.3	9.8	5.9	2.9
800	42.3	39.5	35.1	29.1	21.4	15.2	10.5	6.4	3.1
1000	44.9	41.4	36.8	30.4	22.5	16.1	11.2	6.9	3.4
1200	47.5	43.4	38.4	31.8	23.6	17.0	11.9	7.4	3.7
1400	50.1	45.4	40.0	33.1	24.7	17.9	12.6	7.9	4.0
1600	52.7	47.4	41.6	34.4	25.8	18.8	13.3	8.4	4.3
1800	55.2	49.4	43.2	35.8	26.9	19.7	14.0	8.8	4.6
2000	57.8	51.4	44.8	37.1	28.0	20.6	14.6	9.3	4.9
2200	60.4	53.4	46.5	38.5	29.1	21.5	15.3	9.8	5.2
2400	63.0	55.4	48.1	39.8	30.2	22.4	16.0	10.3	5.4
2600	65.6	57.3	49.7	41.1	31.3	23.3	16.7	10.8	5.7

Table 9

Values of $-\Delta G_{\text{mix}}^{\theta}$ in kcal mol⁻¹ as a function of x_2 and temperature

Temp/K	$x_2 = 0.1$	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	372	343	375	380	387	392	396	400	402
200	350	352	355	360	367	372	377	380	383
400	333	335	338	344	351	357	361	365	367
600	315	318	321	324	335	341	345	349	352
800	298	301	305	311	319	325	330	334	337
1000	278	282	286	292	301	307	312	316	320
1200	260	264	269	275	283	290	295	300	303
1400	241	246	251	258	266	273	278	283	287
1600	221	227	232	240	248	255	261	266	270
1800	203	209	215	222	231	238	244	249	253
2000	184	191	197	205	214	221	228	233	237
2200	165	172	179	187	196	204	210	215	220
2400	146	154	161	169	179	187	193	199	204
2600	126	135	142	151	161	169	175	181	186

The points in table 9 are plotted in figure 3 together with that for the half reaction (b), and the minimum temperature for the reduction of aluminium oxide by charcoal in the presence of copper summarised in table 10.

Table 10

Minimum temperature of reduction of Al_2O_3 in the presence of copper

x_2	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Temp/K	1882	1925	1960	2017	2080	2125	2167	2205	2235	2280

If $x_2 = 0.1$, the Cu-Al alloy contains 4.5% Al and the temperature of reduction is 1609°C.

This calculation confirms the experimental observation of Yang Gen¹⁴ that heating a mixture of aluminium oxide, powdered copper and charcoal, with borax as a flux, gives an alloy containing some aluminium. The temperature of reaction was about 1600°C. However, as can be seen from the data in table 10, in order to obtain an alloy containing 85% aluminium, a temperature of at least 2000°C is required.

Recalling the temperature that could have been attained in Jin dynasty China, it is just possible that an alloy with a low aluminium content could have been prepared, but not one with a high aluminium content such as 85%, as was suggested by the archaeological evidence.

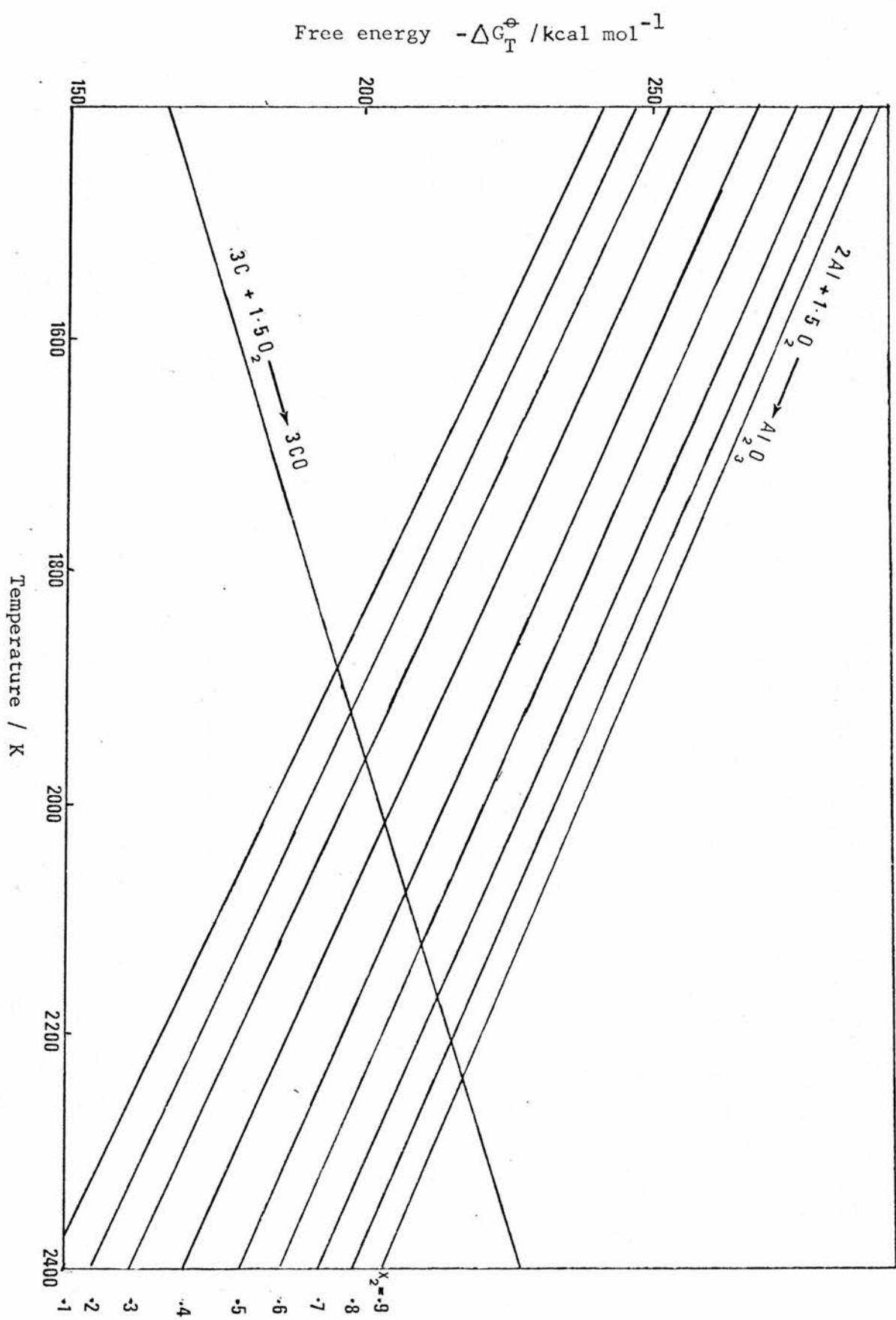


Figure 3 : Reduction of Al_2O_3 in the presence of Cu (x_2 = mole fraction of Al)

While this work was being carried out a completely fresh series of detailed analyses of the pieces of buckle had been carried out by a different research group. One of the samples was shown to be a Ag-Cu alloy, while another sample was shown to have aluminium as the main constituent. This time, however, the results diverged from those previously found in that, the piece was aluminium containing about 1% impurities (principally iron and only 0.2% copper). In the light of this analysis further doubt was thrown on the authenticity of the Chinese finds, as well as the results and techniques of the previous researchers. The question of the authenticity of the metal had to be looked at much more closely.

Microscopic analysis on the latter was used to try to determine whether the piece of metal of this kind was ancient or modern. The photomicrograph also did not reveal the structure of an Al-Mn alloy with 10% copper and 5% manganese, again disputing the results obtained initially. It revealed a structure which could be considered homogeneous. Even from the microstructure of the metal it was difficult to prove that it was actually an ancient metal. Certainly it did not resemble the direct products of present day industrial electrolysis. Another aspect arose when the corrosion resistance of an aluminium alloy is considered. According to analysis the belt ornament pieces would be a rich alloy as far as its aluminium content was concerned, with little copper. Such alloys are very corrodable. The resistance to corrosion of the objects

found seems to indicate that it is a question of alloys of the type bronze or aluminium, ie a maximum of 10% aluminium.

Taking this into consideration, it is perhaps not so easy to believe that such a small object could be buried in an underground tomb for 1655 years, without entirely corroding away, and what is more maintaining a silvery-white colour.

What sort of protection could it have had? No other aluminium objects of that period have been found. These facts together, make the occurrence of the aluminium alloy appear highly improbable.

From the archaeology and the history of the tomb, and the situation where the silver belt ornaments (photograph 1) were found, it was confirmed that they were indeed left there in the third century. As to the authenticity of the Chinese finds regarding the small fragments of aluminium, in view of the recent, more reliable, analytical data, and the fact that the tomb in the immediate vicinity had been rifled several times, it is now firmly believed that they are not of ancient origin. Rather they may have been introduced into the tomb before the scientific excavations of the tomb began, and as such are most likely intrusions.

Therefore the calculation and historic survey both firmly point to the lack of authenticity of the finds. Where,

initially archaeology could not decide, chemistry could. However before concluding it should be pointed out, that the Chinese claim was not an absurd one, even if somewhat unlikely, in view of the advanced state of Chinese metal technology, and the abundance of aluminium ore. One can only wonder, perhaps unprofitably, how near the Chinese came to making aluminium alloys.

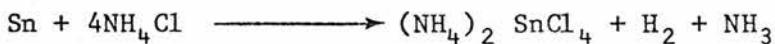
CHAPTER 3

The Preparation of Mosaic Gold

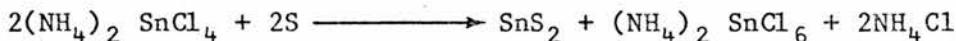
In the crystalline form tin (IV) sulphide looks very like gold, hence its old name of mosaic gold or aurum musivum. Accounts of its preparation from tin amalgam, sulphur and sal ammoniac (NH_4Cl) are fairly common in alchemical texts.²⁸ The earliest known European recipe for the preparation of mosaic gold is in an anonymous, untitled manuscript catalogued as De Arte Illuminandi in the Biblioteca Nazionale in Naples. The translation of this version of the recipe has been discussed by Partington.²⁹ Both Davy³⁰ and Berzelius³¹ showed that the product of reaction was tin (IV) sulphide, but the mechanism of reaction is still unknown. In the West, the first investigation into the methods of preparation of tin (IV) sulphide is thought to be that of Woulfe.³² He studied the reaction extensively and has given many recipes which resulted in the formation of tin (IV) sulphide. From these he has demonstrated that mercury is not necessary for the formation of tin (IV) sulphide, since a mixture of tin, sulphur and ammonium chloride would also give it. According to Lagutt,³³ ammonium bromide could be used instead of the chloride, and he concluded that the halogen of the ammonium halide was the active agent. Heating a mixture containing tin and sulphur only, does not result in the formation of SnS_2 unless the reaction is conducted at high pressure.³⁴ At normal pressure, the presence of ammonium chloride is essential for SnS_2 formation. Since

the exact role of ammonium chloride in the reaction has not been proved, it was decided to begin the study of the formation of tin (IV) sulphide with an investigation of this reagent.

In the preparation of SnS_2 from sulphur, ammonium chloride and tin, Gmelin³⁵ assumed that the first step in the reaction is formation of ammonium chlorostannite:



The formation of hydrogen in this manner is unexpected. According to Gmelin³⁵ as the temperature rises further, the sulphur reacts with the ammonium chlorostannite, forming SnS_2 :



This proposed reaction scheme is unsubstantiated by any experimental evidence for the formation of a compound ammonium chlorostannite. Indeed, no evidence could be found in the literature for such a compound. Using an experimental approach, we attempted to test the validity of the reaction scheme put forward by Gmelin³⁵.

Initially a mixture of ammonium chloride and tin was heated together in a covered crucible for two hours to

determine if any ammonium chlorostannite was formed. There was no apparent reaction. The ammonium chloride sublimed each time the experiment was attempted. The residue was boiled in water and tested for the presence of tin in solution. A negative result was obtained. Therefore tin was not found to be present in an anionic form in solution.

Subsequently a mixture containing tin, sulphur and ammonium chloride, in the proportions recommended by Woulfe³² was heated for two hours. The experimental set up illustrated in figure 1 permitted gases evolved as a result of the reaction to be collected and tested for the presence of hydrogen.

During reaction a yellow solution appeared in drechsel bottle (b). The gas collected in the test tube was tested however it appeared that only air originally in the system was present. A strong odour of hydrogen sulphide was noticed. To the solution in bottle (b) thought to be ammonium sulphide, sodium hydroxide was added, and the resulting solution tested for the presence of sulphide using two separate methods: (i) lead acetate solution (ii) sodium nitroprusside solution. Reaction of the test solution with lead acetate solution resulted in a black precipitate of lead sulphide. Reaction of the test solution with sodium nitroprusside gave a purple colouration indicating the presence of sulphide. Both these simple tests indicated sulphide was present.

The reaction flask (1) which initially contained tin,

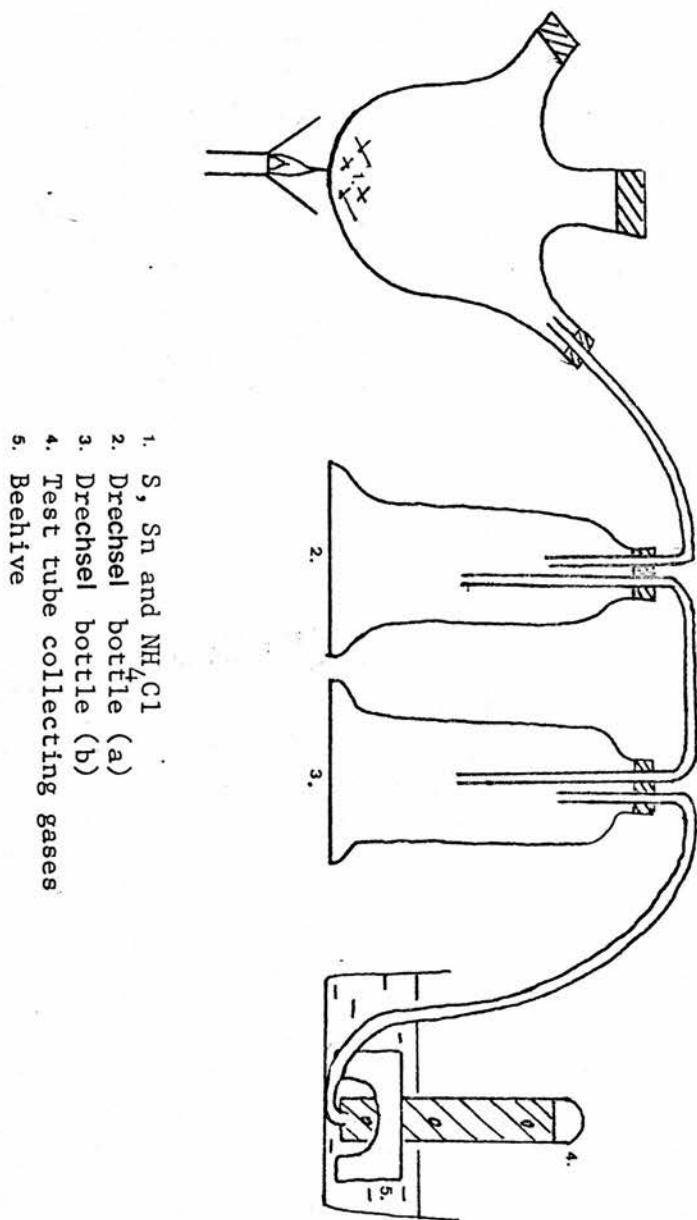


Figure 1 : Beehive experiment

sulphur and ammonium chloride was found to contain three very definite layers. The uppermost one comprised mainly unreacted sulphur and ammonium chloride, which had sublimed and condensed around the top of the flask. The second layer consisted of glistening gold-coloured plates. Beneath this the third layer was composed of grey metallic material (either unreacted tin or tin(II) sulphide, SnS_2). At this stage, we thought it important to verify that the second layer was SnS_2 . Attempts to purify some of the gold coloured crystals, by sublimation was unsuccessful. However X-ray powder diffractometry was carried out on the crude sample, as well as on some commercial SnS_2 . X-ray diffraction in chemical analysis enables the diffraction pattern from the crystalline solid to be examined. The X-ray was taken without further treatment.

The system of tin (IV) sulphide, is currently filed under PDF card 1-1010. Because of differences due to lower symmetry, and crystal form, additional lines in the pattern have been found.^{36,37} SnS_2 is thought to exist in two and possibly three modifications. Phase transitions are fully described here.³⁷ The results are tabulated below for (i) sample material (ii) commercial SnS_2 and (iii) values taken from PDF card No. 1010.

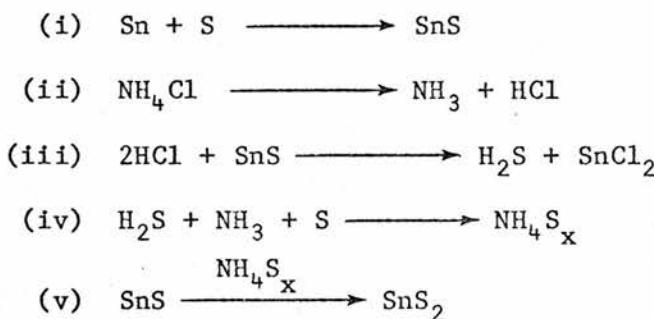
Sample CuK α_1 radiation			Commercial SnS ₂ CuK α_1 radiation			PDF No.1010 (SnS ₂) CuK α_1 radiation		
20°	dÅ	I	20°	dÅ	I		dÅ	I
15.0	5.90	100++	15.1	5.86	100++		5.90	50
26.6	3.34		26.7	3.33			3.14	
28.3	3.15		28.4	3.14			2.77	100
30.4	2.94	74	30.45	2.93	72		2.14	50
32.2	2.78		32.3	2.77			1.82	
33.9	2.64		34.0	2.63			1.74	
41.9	2.15		38.1	2.36			1.66	
46.2	1.96	100	42.0	2.15			1.57	
50.0	1.82		46.3	1.96	100		1.52	
51.8	1.76		50.1	1.82			1.469	
52.5	1.74		51.85	1.76			1.388	
55.0	1.66		52.6	1.74				
63.0	1.47	77	55.1	1.66				
			63.2	1.47	79			

The data from (i) and (ii) are almost identical and in turn both compare well with the data from (iii), although it appears that other crystalline material is present in (i) and (ii). From this, it is certain that SnS₂ is present in the sample material.

Therefore, as Gmelin³⁵ and others have stated, the reaction between tin, sulphur and ammonium chloride does furnish SnS₂. However, no evidence was found to substantiate the scheme proposed by Gmelin involving the intermediate formation of ammonium chlorostannite and hydrogen.

We suggest that the key role of ammonium halide is formation of ammonium polysulphide which can convert SnS into

SnS_2 , a step known to occur in a scheme widely used for inorganic qualitative analysis.³⁸ Tin and sulphur react on heating to form tin (II) sulphide, and this in turn, would react with gaseous HCl to form H_2S . Also H_2S , NH_3 and S react to form ammonium polysulphide (NH_4S_x)³⁹ and the oxidation of SnS to SnS_2 can then be effected. The reaction scheme proposed is:



The only salt that could bring about such a reaction is an ammonium salt of a strong acid. The ammonium chloride was concluded not to be acting as a flux since even in the presence of mercury, it greatly enhances the reaction. Other indications to substantiate this will be commented on later.

Several of the steps in this reaction scheme were examined in order to provide some experimental verification.

Although the reaction (iii) is documented,⁴⁰ we set up an experiment to test it for ourselves. A steady stream of hydrogen chloride gas was passed over glass rings coated with tin (II) sulphide. After ten minutes had passed, a strong odour of hydrogen sulphide was apparent. To verify this the gases obtained were bubbled through lead acetate

solution and a black precipitate resulted indicating the presence of sulphide. We concluded reaction (iii) does occur.

Considering our scheme, a reaction between ammonium chloride and tin (II) sulphide should also give hydrogen sulphide gas and tin detectable in the solution. To test this a mixture of ammonium chloride and tin (II) sulphide was heated. A slow steady stream of nitrogen was passed over the mixture throughout the course of the experiment, and the resulting gases bubbled into lead acetate solution. As expected a positive result for sulphide was obtained. The product remaining in the reaction vessel after completion of the reaction was then boiled in water and tested for the presence of tin by the following procedure:

The solution under test (10 ml) was made 0.5M in HCl and placed in a 20 ml volumetric flask. To this solution, concentrated HCl (2 ml), 1% sodium lauryl sulphate (0.5 ml) and 4-methyl-1,2-dimercaptobenzene (dithiol)⁴¹ were added, thoroughly mixing after the addition of each reagent. Simultaneously a blank containing 0.5M HCl (10 ml), in place of the test solution, was run, the other reagents being added as above. Both flasks were stoppered and placed in a water bath at 60°C for ten minutes. These were then cooled to 20°C and made up to volume with distilled water.

If tin is present in solution form, dithiol gives a red lake which is held in suspension by the sodium lauryl

sulphate. The product from heating tin (II) sulphide and ammonium chloride gave a pink coloration. Since both tin (II) sulphide and tin (IV) sulphide are viturally insoluble in the test solution and tin itself does not form hydroxides in acid media, the pink colouration is most likely to be a result of the presence of tin (II) chloride. Both a blank and tin (II) chloride solution were also tested for completeness.

Table 2 Dithiol tests

Sample solution	result obtained
Blank	clear solution
SnCl_2 (control)	pink coloration
product from heating	pink coloration
$\text{SnS}, \text{NH}_4\text{Cl}$	

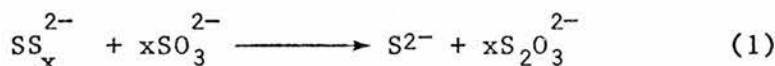
This confirms reaction (iii) in the proposed scheme is possible.

Perhaps more interesting is the likelihood of step (iv) the formation of ammonium polysulphide. By heating ammonium chloride, hydrogen sulphide and sulphur together and the resulting product collected, any polysulphide formed should be detectable using an appropriate analytical technique.

The analytical methods for polysulphide determination have evolved from essentially gravimetric procedures, to classical titrimetry and more recently to potentiometric titrations. Sulphur reacts with an alkaline solution to produce sulphate, polysulphide and thiosulphate and as a result of this there are many cases which involve

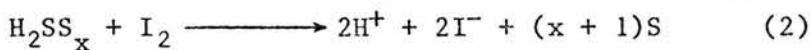
these three species together. Many of the older basic reactions used for separating and differentiating between the various species, are still in current use. The analytical chemistry of polysulphide has been reviewed by Algren *et al.*⁴². A number of methods has been developed with the resulting species being determined by the usual iodometric,⁴³ potentiometric⁴⁴ or acidometric titrations. The more common analytical procedures are based on one or more of the ten established reactions⁴⁵ now summarised.

Alkali and ammonium polysulphide have the general formula M_2S_x where $x > 1$. Polysulphide sulphur reacts with sulphite in neutral solution at 50°C to form thiosulphate,

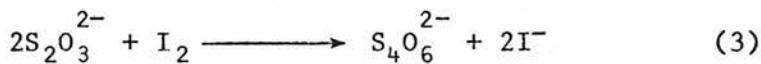


and so via the thiosulphate renders polysulphide measurable by iodometric titration.

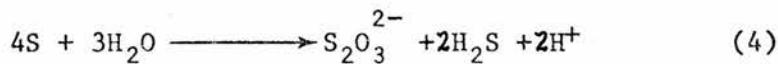
The monosulphide moiety of polysulphide can be quantified by a similar titration since it is oxidised by iodine in acid medium



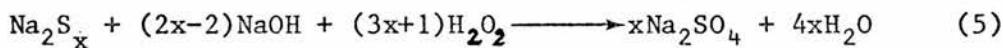
Thiosulphate is also oxidised by iodine enabling a similar analysis.



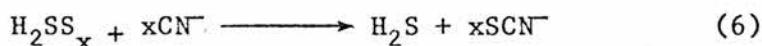
Both elemental sulphur and polysulphide sulphur can be assessed in the form of thiosulphate since they are hydrolysed by hot water to give hydrogen sulphide and thiosulphate.



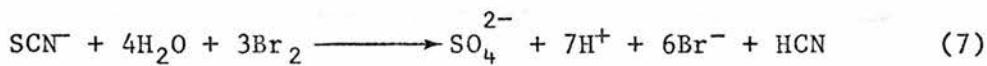
The total sulphur content of polysulphide can be measured by oxidation with alkaline peroxide solution. The excess of alkali is back titrated with standard sulphuric acid.



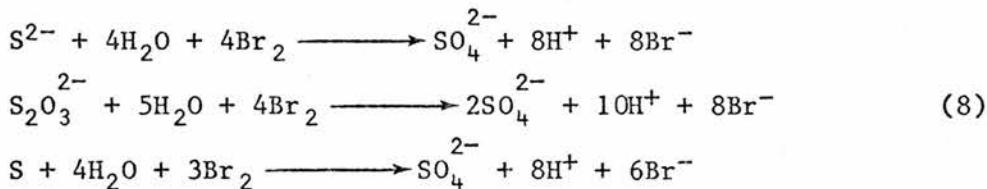
Polysulphide reacts with thiocyanates and cyanide; one thiocyanate for each polysulphide-sulphur atom.



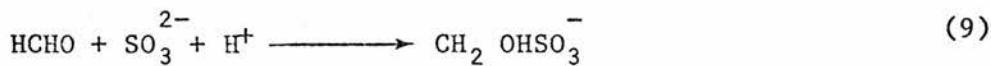
The thiocyanate is oxidised by bromine, but not by iodine in acid medium, the final bromide content then reflecting the original polysulphide component.



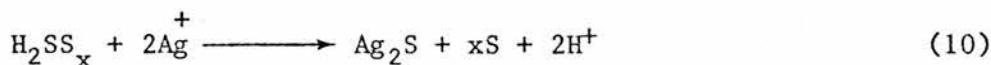
In a similar fashion although iodine only oxidises (2) and thiosulphate (3) in acidic medium, bromine or hypobromite oxidises both these and polysulphides to sulphate.



When present with polysulphide, sulphite may be masked by formaldehyde and the polysulphide determined without interference:



The monosulphide moiety of polysulphide can be measured indirectly by argentometric methods



For this work it was decided to adopt an analytical technique which was both recent and had proved successful in investigating materials similar to the mixture of products obtained from our experiments. The procedure described by Satake et al⁴⁶ for the analysis of blast furnace slag seemed appropriate. The ions were determined potentiometrically with a standard silver nitrate solution. The three species polysulphide, sulphide and thiosulphate were determined from two titrations for each sample. If satisfactory results could be obtained with a polysulphide stock solution, then we could apply the method to our reaction mixture. In order to proceed it was first necessary to make both a silver-silver sulphide ($\text{Ag}-\text{Ag}_2\text{S}$) and a silver-silver iodide electrode ($\text{Ag}-\text{AgI}$). These were prepared by the thermal electrolytic method briefly described below.

Conductivity water was used in all purifications. This was further distilled to minimize the contamination hazard of organic or related impurities. A paste of high purity silver oxide was required for the preparation of the thermal electrolytic electrodes. An important precaution taken in the purification, was the thorough washing of the resulting precipitate from the reaction between silver nitrate and sodium hydroxide. By soxhlet extraction with conductance water all water soluble impurities were removed. The silver oxide obtained is dark brown in colour. The electrodes were cleaned by boiling in concentrated nitric acid, followed by

repeated rinsing in distilled water and finally boiled in conductance water. Several thin coatings of silver oxide were then applied as a water paste to the three turn platinum spirals of the electrodes. In order to preclude the possibility of sputtering by the rapid formation of steam, the electrodes were maintained in the furnace at about 100°C for thirty minutes to permit superficial drying. The temperature was then raised to 450°C, at which it was held for a further thirty minutes. The electrodes were left to cool in the oven to avoid thermal shock. This was repeated to give several coatings on the electrodes. The electrodes were then ready to be anodized.

For the iodide electrode, a 0.1*N* potassium iodide was used to effect the anodic deposition of the halide layer. A current of 10mA from a constant current source was passed through the circuit for thirty minutes. After rinsing with conductance water the electrode was stored in a foil covered quick-fit test tube. The fresh electrode was yellow in colour. To form the sulphide coating, the electrode was anodized in a 1M solution of sodium sulphide.⁴⁷ The washed electrode was stored in a dilute sulphide solution. Table 3 summarises the conditions used to test the electrodes.

Table 3

Ag-AgI vs S.C.E.	0.1M iodide solution titrated with standard silver nitrate.
Ag-AgI vs S.C.E.	thiosulphate solution titrated with standard iodine solution
Ag-Ag ₂ S vs S.C.E.	0.01M sulphide solution titrated with standard silver nitrate
Ag-Ag ₂ S vs S.C.E.	* 5×10^{-4} M sulphide solution titrated with standard silver nitrate.

*This was the concentration range employed by Satake *et al*⁴⁶ and would provide a check on the recoverability of the electrode in such a dilute solution.

At this stage both the Ag-AgI and Ag-Ag₂S electrodes appeared to be functioning sufficiently well to proceed with the determination of polysulphide in a stock solution, in the manner described by Satake *et al*.⁴⁸

After repeated trials, the expected results were not observed. A source of error was found in the description for the preparation of the polysulphide stock solution⁴⁸ and subsequently corrected. The experiment was repeated and an end-point was obtained using the Ag-Ag₂S electrode. However, upon changing to the Ag-AgI electrode, no end point corresponding to the sulphate ion was observed. As this electrode is prone to degenerate over a short period, further

testing of the electrode verified that this had in fact occurred. Much time was spent trying to re-make this electrode with no success. The recommendation by Taniguchi and Janz⁴⁹ was that the best silver-silver halide electrodes were obtained when the electrolysis was controlled. Too thick a coating of silver halide tended to make the electrode very sluggish and added little to its stability. The importance of the colour and porosity relative to the attainment of stable silver-silver halide electrodes, that equilibrate rapidly, was also underlined. Obviously in our case the optimum conditions were not found.

An alternate method for the determination of polysulphide was used.⁴³ This method, developed for the titrimetric determination of alkali polysulphides describes how sulphide and polysulphide are separated from thiosulphate, by treatment with an ammoniacal solution of zinc sulphate. Polysulphide is determined in accordance with the equations:



The thiosulphate is determined iodimetrically in the filtrate from the precipitate of zinc sulphide, and sulphide is determined indirectly by iodometric titration of the alkali polysulphide solution. The total sulphur is determined in a separate sample by oxidation with bromine water, precipitation by barium ions, a standard barium chloride solution being

added to the sulphate solution. The excess barium ions are then determined using the disodium salt of EDTA, with the dye eriochrome black T as the indicator.⁵⁰ The experimental procedure given by Legradi,⁴³ was followed using a polysulphide stock solution prepared by dissolving about 27g of sulphur in a 100g portion of 37.7% solution of sodium hydroxide at 100°C and this was stored under paraffin to prevent aerial oxidation. the following table 4 shows the results obtained.

Table 4 Results for alkali polysulphide stock solution

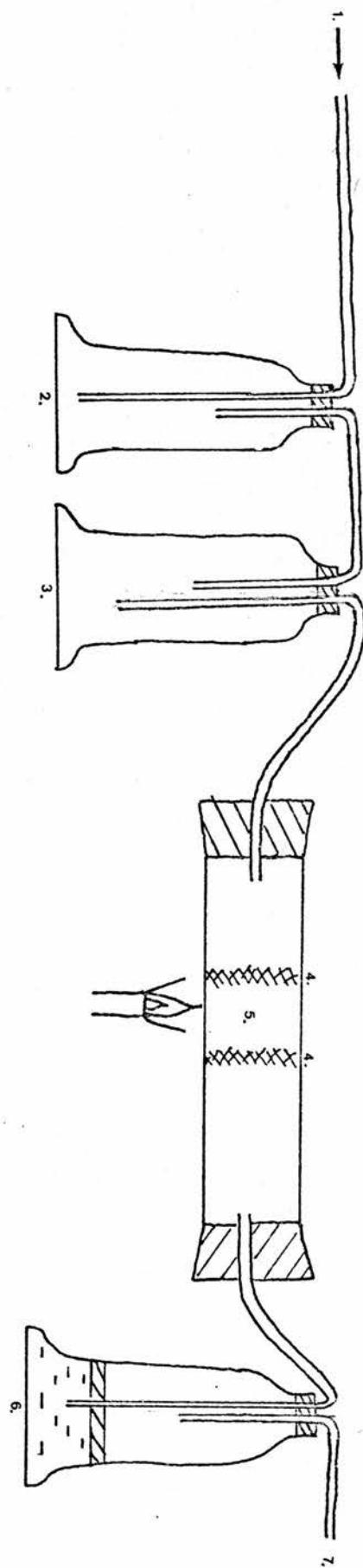
polysulphide-S	thiosulphate-S	sulphide-S	total-S
13.22g	7.62g	5.20g	26.45g

Following on from this, since we are trying to show that a reaction between ammonium chloride and sulphur in the presence of hydrogen sulphide, will produce ammonium polysulphide, the experiment in figure 2 was set up and the resulting solution analysed by this Legradi method.⁴³

Table 5 Results for test solution

polysulphide-S	thiosulphate-S	sulphide-S
6.6g l^{-1}	0.17g l^{-1}	1.56g l^{-1}

From this it is clear, that one may assume ammonium polysulphide will be formed during a reaction between tin, sulphur and ammonium chloride. This ammonium polysulphide will, in turn, bring about the oxidation of tin (II) sulphide to tin (IV) sulphide. Thus the reaction scheme we have proposed appears to be a feasible explanation to the reaction occurring between tin, sulphur and ammonium chloride.



1. Hydrogen chloride gas
2. Bubbler
3. Safety flask
4. Glass wool plugs
5. NH_4Cl and S
6. Flask containing an aqueous solution covered with a layer of paraffin
7. Fume cupboard

Figure 2 : Experiment to determine the presence of polysulphide

We found also that reaction is effected by other ammonium halides. As the halogen of the ammonium halide is considered to be the active agent, it was reasonable to assume that similar reactions with ammonium bromide and iodide would occur since all ammonium salts volatilize at around 300°C. The vapour of the sublimed salt is largely dissociated into ammonia and acid. Three experiments were run under the same conditions. The number of moles of the ammonium halide used was the same in each experiment. Therefore any differences observed in the products, could be attributed to the use of the different ammonium halides:

(a) tin, sulphur, ammonium chloride (b) tin, sulphur, ammonium bromide (c) tin, sulphur, ammonium iodide.

Visually the product obtained from (c) 'glistened' the most and contained less amorphous material than either (a) or (b). It is very difficult to quantify beauty, although a millihelen, the unit of beauty used by Paul Jennings is a possibility, but not one we could employ here. Instead the use of a scanning electron microscope was used which enabled photographs to be taken of the three products and allowed a closer look at the crystal of tin (IV) sulphide.

An electron beam striking a spot on the specimen produces secondary electrons. These are collected and amplified. This amplified signal passes to the cathode ray tube, where it appears as a spot. This signal is from one

spot on the specimen. The beam is scanned over the surface of the specimen by the microscope, each spot producing a corresponding spot on the cathode ray tube screen. Thus the object of image is divided into many picture elements (1000 lines of 1000 spots/line, ie 1 000 000 spots), and this point to point correspondence will cover the image by means of sweeps of electron beam on the surface of the specimen, and simultaneous sweeps of the cathode ray tube beam to produce a visual image. The photographs taken, numbered sample 2 $\text{Sn}, \text{S}, \text{NH}_4\text{I}$ sample 3 $\text{Sn}, \text{S}, \text{NH}_4\text{Br}$ and sample 4 $\text{Sn}, \text{S}, \text{NH}_4\text{Cl}$ were taken at various magnifications. The platelets were arranged less orderly and contained far more amorphous material in sample 4, than in either sample 2 or 3. The platelets in sample 2 were distinctly larger than the other samples. Sample 2 also, was virtually free of amorphous material. Since iodide decomposes at a lower temperature, one might expect more polysulphide formation and hence more tin (IV) sulphide. As hydrogen iodide is a weaker acid than hydrogen chloride or bromide, precipitation would be slower giving rise to these large platelets. Although further analysis was not undertaken it is possible to state that ammonium iodide did furnish the most beautiful preparation of tin (IV) sulphide.

As previously stated there is the possibility that the ammonium halide could be acting as a flux. However, one would not expect ammonium iodide to be effective solely as a flux, since it will not clean tin oxide off the surface like a flux.

In the light of this work on tin (IV) sulphide preparation, we concluded tht the reaction scheme proposed by Gmelin for the reaction occurring between a mixture of tin, sulphur and ammonium chloride is wrong. Instead a mechanism of the form we have proposed is consistent with the experimental data.

Tin (IV) sulphide sometimes known as mosaic gold was one of the most successful of early laboratory syntheses in European chemistry, but it had been known in China by the Chinese alchemists many centuries before its European debut. Why were these early alchemists interested in mosaic gold? An answer to this can be found by looking at the history of Chinese alchemy. European alchemy is well known to have concerned itself intensively with base metal to gold transmutation. The emphasis in Chinese alchemy on this matter is even greater. Chinese alchemy is however, far from being identical with Western. In both we find the idea of transmutation and the making of "gold" but the many stories of Chinese alchemy are significant, in as much as they reveal that gold to the Chinese was not a medium of currency but an imperishable substance. The whole emphasis of the Chinese alchemist is upon the making of gold as a substance to confer longevity or immortality upon the body, an idea which does not appear to enter Western alchemy until the Islamic period. Commercial pursuits in early China were despised which perhaps explains the scarcity of accounts of attempts at the

alchemical preparation of gold for mercenary purposes; the prolongation of life on the other hand, was a noble aim to which artificial gold should be solely devoted. It was believed that artificial gold was a substance of such potency, that eating and drinking from vessels made of it, would be conducive to longevity. We thus see at the outset, a difference of intention between the Chinese and Western alchemy.

The evolution of Chinese alchemy is remarkable, since at a period some two or three centuries before the earliest Greek writings on alchemy, there appeared in China accounts of beliefs and processes which must be called alchemical. These alchemical writings can be described by two terms, *aurification*, the conscious imitation of gold, often with intent to deceive and *aurifaction*, the belief that it is possible to make gold from quite different substances.⁵¹ There are many charming legends about the early masters of Chinese alchemy which serve at least to show the attitude of their successors towards the origin of the art. An example is the story of Wei Bo-yang⁵², who lived in the present province of Kiangsu about 120 A.D. The story tells how he entered the mountains to make efficacious medicines with three *disciples*, and shows his great dedication to his cause. Not just a few among the early Chinese lived, withdrawn, deep in the mountains to seek out the secret for making the golden elixir of immortality.

Chinese alchemy is closely bound up with Daoism, a system of philosophy and religion which was based partly on the teachings of Lao-Tsu of sixth century B.C. and given form and direction by Chang Tao-ling in the second century A.D.

Dao (道) means the way or path. Its attention was focussed on spiritual exercises initially, and later, on the problem of mortality. The Daoists wished for long life, the longer to prepare themselves for paradise. By a natural evolution, the desire for longevity grew into the hope of immortality, and the disciplines of the cult were thus led to the study and practice of alchemy. The Daoist canon is a rich repository of ancient alchemical writings.

In China, perhaps the earliest known treatise of a purely alchemical character is the Can Ton Qi, written by Wei Bo-yang about 142 A.D.⁵², Wei Bo-yang who has been called the 'father of Chinese alchemy', was a Daoist philosopher alchemist. This deals with the preparation of a medicine, "capable of making living beings immortal". Wei Bo-yang states that, "men of art by feeding on gold attain longevity". Its contents show that an established alchemical tradition existed in China by this period. In an interesting introduction to the English version of Can Tong Qi, Davis⁵³ points out that the Chinese alchemy is based upon the two fundamental ideas of the five elements and the two contraries (Yin-Yang). The five elements which were recognized as early

as the twelfth century B.C. are, water, fire, wood, gold (or metal) and earth. These were correlated with the five virtues: tastes, colours, tones, seasons and numerous other quintets. Yang and the sky are masculine and their element is fire, whereas yin and the earth are feminine and their element is water. By their interaction the two contraries were held to give rise to the five elements constituting the material of the world. This doctrine of the two contraries, or reciprocal principles of nature, found a place under different names, in the mythological systems of all the ancient civilisations.

The methods of attempting the transmutations of metals into gold employed chiefly boilings and fusions and the Chinese were certainly acquainted with sublimation which they used in making mercury from mercury and sulphur. All of these methods made use of yin (water) or yang (fire). The acceptance of alchemical gold as authentic may be due in part to the rarity of gold in China, thus knowledge of its chemical and physical properties would be very limited.

An alchemical manuscript Bao-pu zi (Book of the preservation of Solidarity Master) written by a Daoist called Ko Hung⁵⁴, who lived in south China from 254-334 A.D., the first part of which is entitled Nei Pian or Inner chapters also deals with the transmutations of metals, elixirs of life, ascetic rules for reaching longevity and methods of achieving immortality. Ko Hung gives numerous recipes and points out

that alchemical gold, which is uniform throughout should be distinguished from a base metal superficially tinted to make it look like gold. He states that a man may prolong his life, by taking medicines made from plants, but can become immortal only by the use of a divine elixir made from metals and minerals. It is often difficult to identify all of the substances that were to be employed in the preparation of this elixir, but red and yellow arsenic sulphides, sulphur, cinnabar, alum, salt, white arsenic, oyster shells, mica, chalk and the resins of pine trees were certainly included among the ingredients. The resulting elixir when thrown onto mercury, or a mixture of lead and tin, converted the metal into gold or silver; gold from mercury, silver from the lead-tin alloy. Taken as a medicine for one hundred days it made a man immortal. An interesting detail is that found in this treatise there is a recipe for the conversion of tin into a gold like material. Wu and Davies⁵⁵ first suggested that this material was tin (IV) sulphide. The following is a condensed version of the translation given by Ware.⁵⁶

Ingots of tin are covered with a paste containing red crystal salt, placed in a sealed crucible and heated on a horse dung fire for 30 days. Remove from the fire, the whole interior will look like lime containing clusters of gold beans. Red crystal salt is made by heating equal parts han yan and han shui shi or han yu mie, or bai fan in an iron crucible.

The translation has been modified in two ways. First the last three items in red crystal salt are alternatives rather than components of a complex mixture. Secondly we do not accept Ware's translation of some of the materials, particularly of han yan as amethyst. Three of the ingredients can be identified without difficulty: han shui shi is a mixed sulphate of Ca, Mg, and K; ⁵⁷ bai fan is alum, and han yu nie is alunite⁵⁸ (a basic alum). The identity of han yan is not known from other literary sources. Zi-shi-ying⁵⁹ is the normal name for amethyst and so we find no grounds for accepting Ware's translation.

The essence of Ko Hung's recipe is heating tin with a sulphate (i.e. alum) in the presence of han yan and as a result of this crystals of tin (IV) sulphide are obtained. In such a reaction the oxidation state of sulphur changes from + 6 in sulphate to -2 in tin (IV) sulphide. This reaction we considered initially to be highly unlikely whatever the nature of han yan, and in our first survey of the relevant chemical literature, we could find no precedent. Our initial conclusion was that the recipe had been falsified by Ko Hung to prevent the secret of gold production becoming generally known, however, our experimental studies of recipes from the sixth century manual San-shi liu Shiu Fa for the successful solubilisation of minerals led us to the view that Chinese alchemical texts should be taken very seriously until proved to be erroneous. We, therefore, examined Ko Hung's method

again and made the assumption, merely by comparison with the European recipe, that han yan is ammonium chloride. A sealed container was constructed for these experiments in an attempt to simulate the Chinese recipe as closely as possible. The container is illustrated in figure 3.

The alum was first dried in an over at 420°C for six hours, to remove the water of crystallization. The water of crystallization can be expelled at 300-500°C but 400°C is preferred.⁶⁰ A mixture of dried alum, tin filings and ammonium chloride ~~was~~⁶⁰ then heated together in a crucible contained in the iron vessel at 500°C for five days. Upon cooling and opening fine gold coloured crystals were found to be coating the inside of the iron vessel. These crystals were identified by X-ray powder diffractometry to be tin (IV) sulphide. Further experiments showed that, although ammonium chloride does make the sulphide more crystalline and glistening, it is not necessary for the formation of tin (IV) sulphide. Han yan means 'cold salt' and the well known refrigerant property of ammonium chloride supports the identification. Addition of 10g of ammonium chloride to 100 ml of water lowers the temperature by 15°C. In the north-western provinces of China and in Xin jiang ammonium chloride occurs naturally and under the name nao sha, it is mentioned in the Can Tong Qi of Wei Bo-yang. Therefore it should have been known to Ko Hung working 150 years later. Rather curiously naosha is not mentioned in the Bao-pu zi, although one would have thought its properties

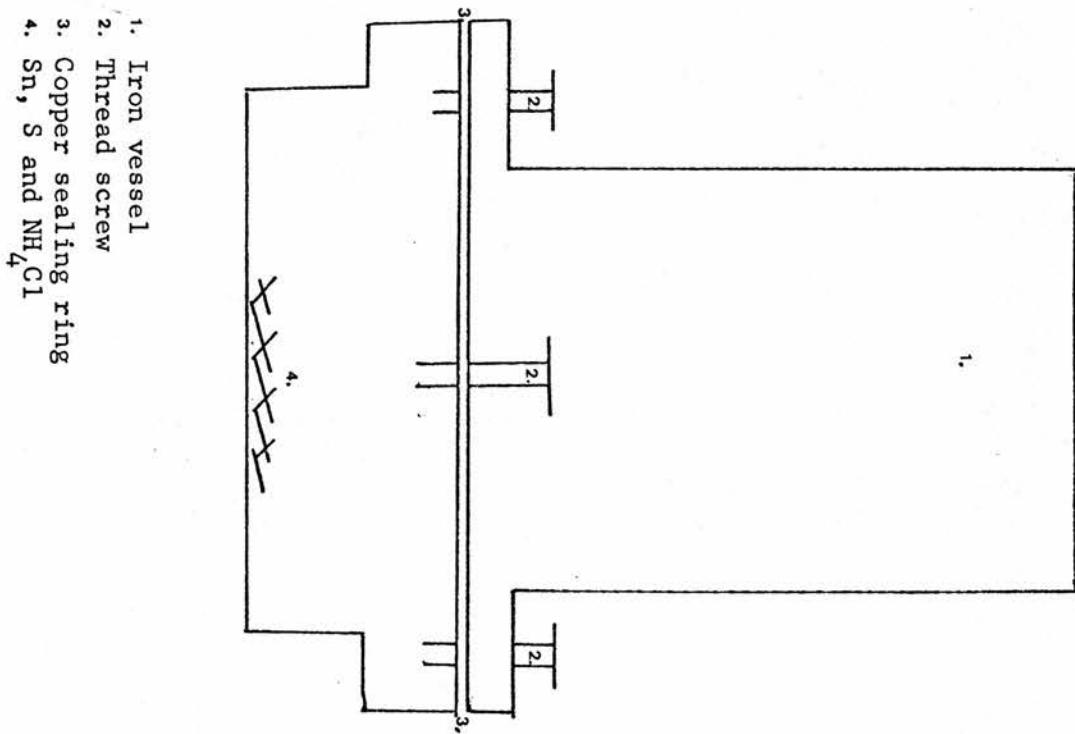


Figure 3 : Diagrammatic representation of the sealed iron container used

1. Iron vessel
2. Thread screw
3. Copper sealing ring
4. Sn, S and NH_4Cl

would have attracted the attention of Ko Hung. We suggest that he knew of it, but under another name.

A further experiment was performed. A sample mixture consisting of dried alum and tin was taken and examined by differential thermal analysis (DTA). The mixture was heated at 5°C/min up to 330°C and then cooled. There was an irreversible, exothermic reaction at 218°C and the product was a dull, dark yellow powder. This temperature is undoubtedly attainable by the horse dung fire mentioned by Ko Hung, although we have no direct experimental evidence on this point. There is no evidence that the role of ammonium chloride in the Chinese procedure is parallel to that for the European recipe. Instead, we suggest that it acts as a flux, cleaning the surface of the tin of its coat of protective tin oxide and making the reaction with alum proceed more readily. Ammonium chloride is used in a number of procedures as a flux.

Finally on this subject the thermodynamics of the oxidation of tin to tin (IV) sulphide on reaction with sulphate was examined by means of an Ellingham diagram.⁶¹ Alum is assumed to be equivalent to $[Al_2(SO_4)_3 + K_2SO_4]$ and the overall reaction divided into the two half equations:



In figure 4 the energies per mole of SO_3 are obtained using the expression

$$\Delta G_T = \Delta H_{298} + \int_{298}^T \Delta C_p dT - T \int_{298}^T \Delta \text{Cp}/T dT$$

with C_p for each component in the form

$$C_p = a + bT + cT^{-2}$$

Numerical values for ΔH_{298} , ΔS_{298} , a , b , and c are taken from the literature.²⁵ Over the temperature range considered (200-800 K) formation of SnO_2 and SnS_2 has a much more negative ΔG than that for the decomposition of $1/3 \text{Al}_2(\text{SO}_4)_3$, hence $\text{Al}_2(\text{SO}_4)_3$ will oxidise tin to the sulphide at all temperatures in this range. These calculations show that formation of SnS_2 is thermodynamically possible; our experiments, and those of Ko Hung, have shown that it is kinetically feasible.

Other data shown in figure 4 have been included for academic interest. For the reaction:



ΔG is also more negative than the decomposition of $\text{Al}_2(\text{SO}_4)_3$ and so the oxidation of hydrogen by $\text{Al}_2(\text{SO}_4)_3$ is also thermodynamically feasible; indeed, it has been reported.¹⁶ The line for the reaction



also lies well below that for the decomposition of $\text{Al}_2(\text{SO}_4)_3$ and so the oxidation of lead, as well as that of tin, is

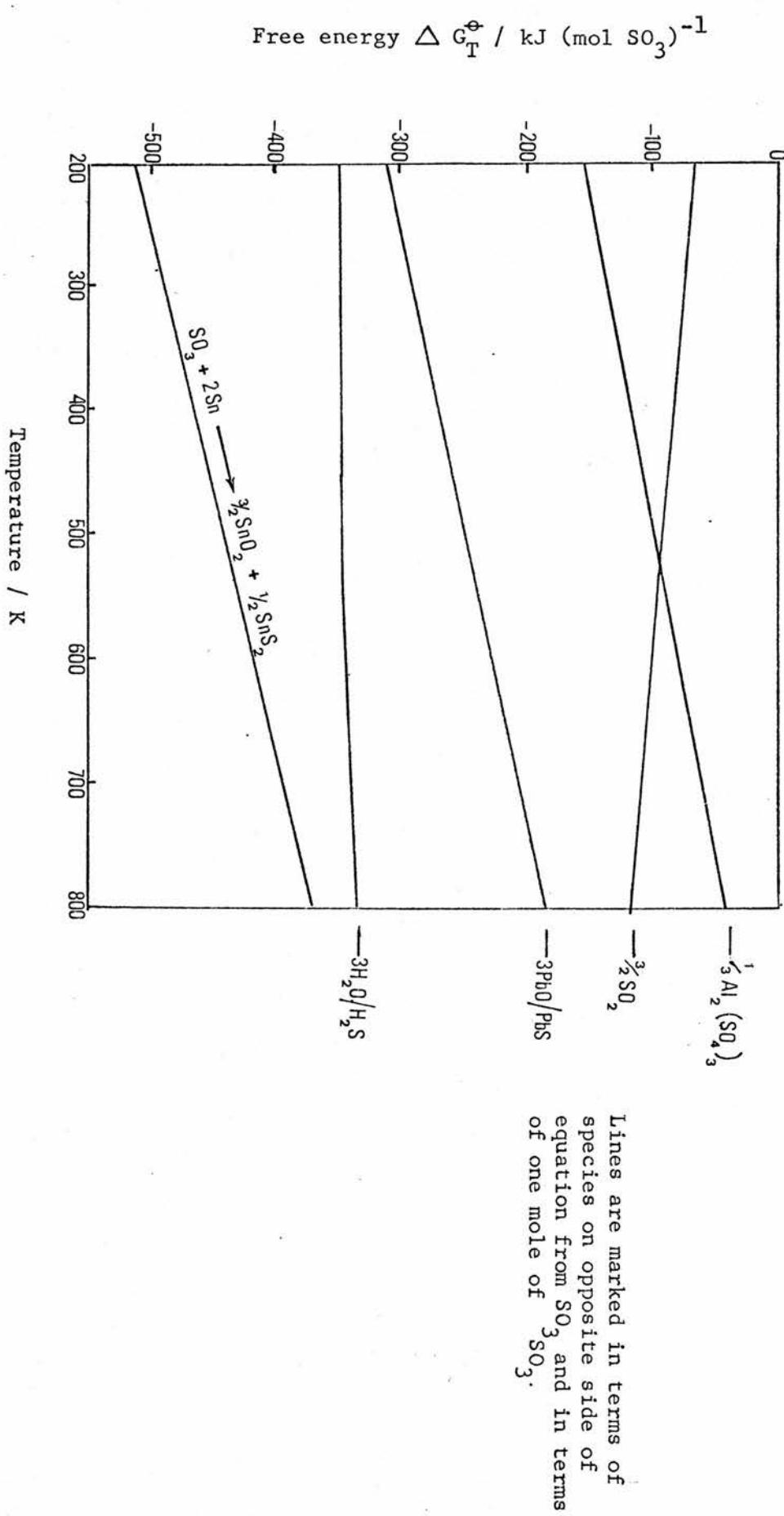
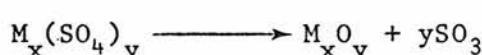
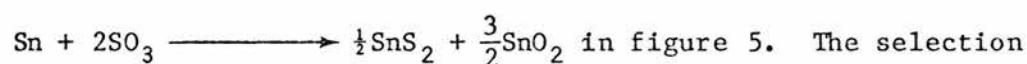


Figure 4 : ΔG^ϕ_T diagram showing that it is feasible thermodynamically from alum to oxidize Sn II Pb and S

thermodynamically possible. A large number of other sulphates were examined by a similar but approximate treatment. The energies per mole of SO_3 are obtained using the expression $\Delta G = \Delta H - T\Delta S$. The free energy curves of the corresponding half equations of the general form

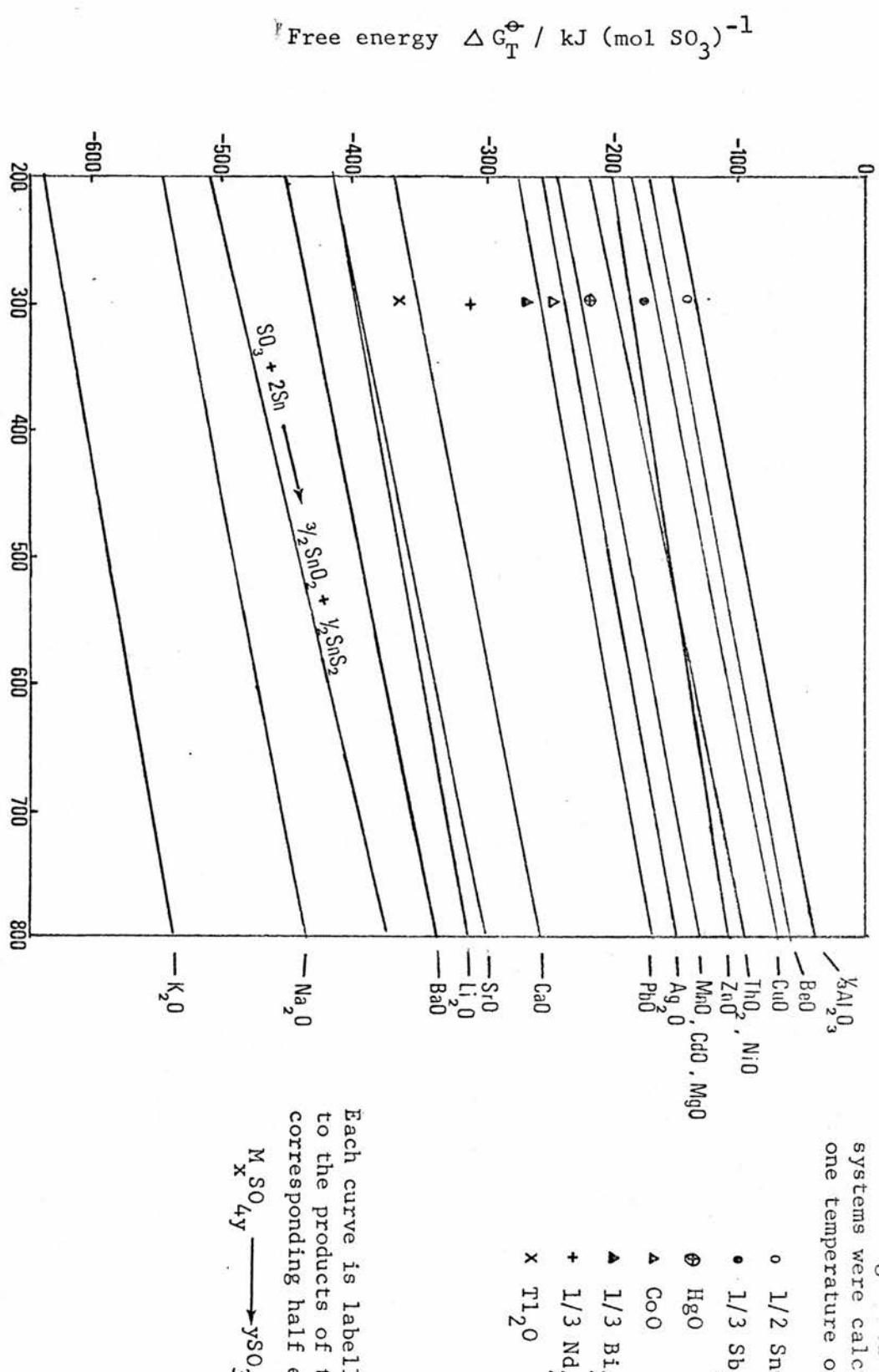


are drawn for comparison with that of the half equation



was governed by the availability of appropriate data, but, as well as Al, the following sulphates according to figure 5 should be able to oxidise Sn to SnS_2 :

Be, Cu, Ni, Zn, Th, Mn Cd, Mg, Ag, Pb, Ca, Sr. Li, Ba Sb, Hg, Co(II), Bi, Na, Tl(I). Only the sulphates of Na, K, Rb, and Cs will not effect reaction and oxidise metallic tin to SnO_2 and SnS_2 . Although many of the theories of Chinese alchemy are not in line with modern understanding, this study provides confirmation of the ability of the Chinese experimentalists.



Free energies of the following systems were calculated at one temperature only

Each curve is labelled according to the products of the corresponding half equation.



Temperature / K

Figure 5 : $\Delta G^\circ-T$ diagram showing which sulphates might oxidise metallic Sn

CHAPTER 4

An Investigation into Sixth Century Alchemical Recipes

It is often supposed that the Chinese alchemists busied themselves mostly with non aqueous reactions of a more or less metallurgical character. Certainly, in the light of the preceding chapters, it can be said that Chinese metal technology was in a very advanced state by 1000 A.D. However, several manuals have survived which describe methods for bringing a number of minerals into solution.⁶² Aqueous solutions of mineral substances were known to Chinese alchemists at least as early as the time of Ko Hung (280-360 A.D.), who gives an account of the preparation of aqueous solutions of realgar and cinnabar.

A later work called the San-shi-liu Shui Fa 三十六水法 (thirty six methods for the bringing of solids into aqueous solution), which was studied by Needham⁵⁹ throws considerable light on the earliest beginnings of the chemistry of inorganic reactions in aqueous medium. Needham published a full translation of this text and dates it about the sixth century A.D. Since printing in China was invented before the eighth century, the copy that survives is probably an accurate reproduction of the original. Chinese alchemical books have none of the obfuscation common to European alchemical manuscripts. The San-shi-liu Shui Fa is written in terse clear language and the instructions for bringing various minerals into solution are precise and unambiguous. In view of the

advanced state of Chinese technology in the sixth century⁶³, it is reasonable to take what is written seriously.

The text itself is in the Daoist patrology and describes how nitre in dilute acetic acid was employed to bring into solution a large number of inorganic substances, the processes being carried out in either porcelein vessels or lengths of bamboo tubing. The latter may have acted in part as semi-permeable membranes. Included in the text is the mention of certain curious phenomena, which were probably the effects of enzymes from organic materials. Therefore, although the making of gold for the preparation of the elixir of immortality was of prime interest to the early medieval experimentalist, it was not the only interest. At the same time, mica and certain other minerals had long been regarded in China as among the substances from which potent elixirs might be made. Therefore to dissolve mineral substances is perhaps a more natural consequence than one might initially think.

The first publication of the San-shi-liu Shui Fa⁵⁹ translation evoked interest among practical inorganic chemists, who made a number of computations suggesting that one or another of the methods translated could not work as they stood.

A later Chinese manuscript makes a very significant statement about the 36 Shui Fa. It says that all the methods depend on the use of nitre for their successful achievement. Although this makes no mention of vinegar, it is clear that in most cases explicit directions are given for its addition.

Thus, although not all recipes mention both nitre and vinegar, the translators strongly suspect that it was the original intention to direct the use of both, but one or the other dropped out in the process of copying. Nitre itself was certainly known at that time; it occurs at least as early as the period of Ko Hung. We can compare this to the West, where the lack of nitre was obviously a limiting factor in the appearance of gunpowder which did not occur until the 13th or 14th century A.D. Gun powder, a primary invention of the Chinese, dates in the East back to the 8th or 9th century A.D. One criticism of the methods pointed out was that one would expect little to happen with such dilute acetic acid, and any nitric acid formed would be of extremely low concentration. The concentrating of acetic acid by distillation is extremely troublesome even with the aid of a column. Therefore, it is unlikely that the acetic acid was concentrated by this technique.⁶⁴ However, there is one way in which acetic acid could have been concentrated in these old days, namely by "freezing out" the water, just as was done for wine and alcohol. The Chinese were able to concentrate dilute ethanol by freezing out to obtain strong spirituous liquor.⁸ This same technique could have been applied to vinegar with the separation of more concentrated acetic acid. The success of this process has been reported more recently.⁶⁴ Since acetic acid and water form a eutectic containing 60% wt/wt acetic acid,⁶⁵ melting point -26°, this is the most concentrated acid which could have been attained by freezing.

The question as to whether some of the methods given are inconceivable under the conditions stated, remains open. I decided the best way forward was to carry out a series of experiments, imitating as closely as possible what the Liang alchemists claimed to do, and consider possible impurities which might be present. Just such a line of work was initiated by Butler et al.⁶⁶ Here, an explanation to the solubilisation procedure for mercury (II) sulphide taken from the San-shi-liu Shui Fa was given. According to the Chinese alchemical procedure, a mixture of nitre and vinegar will bring cinnabar, mercury (II) sulphide, into solution. The conclusion reached was that chloride, generally present in naturally occurring nitre, is necessary for this to occur, and that the copper (II) sulphate present in the recipe catalyses the oxidation of chloride to chlorine.⁶⁶

Following on from the work, two of the translated recipes were given consideration, one concerning the solubilisation of lead, the other concerning the solubilisation of silver. The concentration of these species in the supernatant solution was determined by atomic absorption spectrophotometry.

The application of this technique is very simple and has many advantages over other methods. It is versatile since the availability of lamps for many different analytes provides the analyst with a wide area of application. The absorption method is highly sensitive, it is also almost free of spectral

interference effects. The good reproducibility obtained in practice leads to results of good accuracy and precision.

Like all spectroscopic quantitative analytical procedures, there is a maximum and a minimum to the concentration range of application. The minimum of the range is a function of the detection limits of the element under optimum conditions. The ultimate limiting factor is the noise level of the instrument being used. The maximum of the analytical range is determined by the degree of absorption by the sample. At high concentrations, the degree of absorption is high. Small changes in concentration of the sample produce virtually no changes in absorption by the sample. Hence it is difficult or impossible to measure absorption changes caused by concentration changes in the sample. This is typical of the maximum end of the analytical concentration range.

The necessary calibration of atomic absorption instruments is achieved by means of solutions of known concentration, standard solutions. Standard solutions must be prepared unless a standard addition method is used.⁶⁷ Standards for analytical calibration are generally utilized to prepare a graphical representation of the variation of the analytical quantitative variable measured in the instrument as a function of the concentration. Standard solutions are made to resemble the samples as closely as possible, and the series of standards made up cover the proposed interval of concentrations. the origin of the calibration curve, zero concentration, is

determined by zeroing the instrument with the solvent (blank solution), and re-checking it by measuring the solvent or blank solution. To avoid cross contamination the calibration is started at the lowest concentration range first. Intermediate washing by aspirating water throughout the analysis also helps eliminate this. Calibration curves prepared for immediate analytical purposes are termed working curves. The working curves were repeated in each working session and for each set of sample solutions with the aim of obtaining high accuracy.

The translation of the recipes by Needham et al is as follows:

- (31) 2 lb of lead scrapings mixed with 4 oz of nitre, sealed in (bamboo) tube as before and put in vinegar will form an aqueous solution after 100 days.
- (30) 1 lb of silver, 2 pints of clear wheat sauce, 2 pints of vinegar and 1 pint of wine made from glutinous millet and the fruits of the mu-ching shrub, sealed in a bamboo tube with lacquer and put in vinegar for 30 days will form an aqueous solution.

The terms pound and ounce are translations of the characters jin and liang. Although the actual size of the jin and liang varied in different ages,⁶⁸ there were always sixteen liang to the jin. The relative amount of lead to nitre are therefore known. An experimental investigation of the reaction between lead and alkali metal nitrates in acetic acid was undertaken.

The 100 days mentioned in the recipe suggests that the reaction in vinegar is a slow one. Initially glacial acetic acid was used, in the hope that this would speed up the reaction and thus facilitate the investigation.

The reaction was studied by shaking a solution containing lead in acetic acid with various other reactants. For the experiments using glacial acetic acid, lithium nitrate rather than potassium nitrate was used as the latter is not soluble in the acid. The extent of reaction was calculated from the concentration of lead in the supernatant solution, the latter being determined by atomic absorption spectrophotometry. The term % reaction is used to indicate the fraction of lead present initially which is in solution at the end of the experiment, or at the time specified. Since the presence of chloride was found to be significant in the experiments carried out previously by Butler *et al*,⁶⁶ the effect of this additive was investigated. The working curve was obtained in the way previously described with glacial acetic acid as the solvent.

Table 1 Reaction of Pb(1g) with glacial acetic acid (50 ml)

run no.	LiNO ₃ (g)	other additives	time(h)	ppm lead	% reaction
1	1.5	-	23	240	1.2
2	-	LiCl(1g)	23	11	0.05
3	1.5	LiCl(1g)	23	16	0.08
4	1.5	HNO ₃ (1ml)	23	260	1.3

From run 3, it is seen that the presence of the chloride ion suppresses the reaction, thus the chloride ion is not playing a similar role as that found by Butler *et al*⁶⁶ in their experiments on solubilisation of cinnabar.

Remembering that the Chinese alchemists could have attained only 60% wt/wt acetic acid at best, in order to simulate the recipe in the San-shi-liu Shui Fa, a further series of experiments using acids of this concentration would be more informative to our study. The concentration of lead in solution was as before determined by atomic absorption spectrophotometry. The solvent used was 60% aqueous acetic acid. By convention in figure 1 concentration (the independent variable) is the abscissa. As can be seen, the working curve of concentration against absorbance consists of an almost linear portion near the origin, followed by a section which bends slightly towards the concentration axis. The amount of bend and the point of onset of bend depend upon the amount of absorbable radiation reaching the detector, and on the presence of less sensitive lines within the monochromator band pass. Unabsorbable light may be due to non-absorbing lines from either the source cathode material or the fill-gas which pass within the spectral bandwidth of the monochromator. It also occurs if the ratio of the half-widths of the emission line w_e and the absorption line w_a approaches or becomes greater than unity. Rubeska and Svoboda⁶⁹ showed that the calibration graph can be linear only if w_e/w_a is less than 1/5.

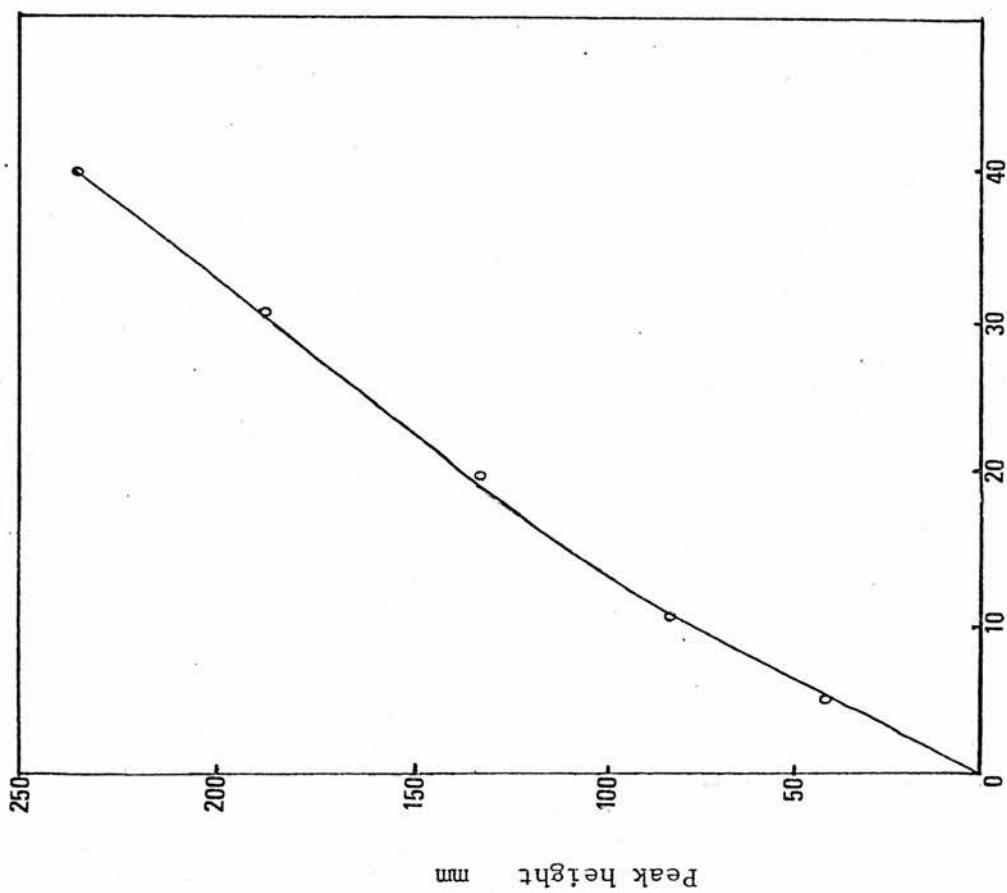


Figure 1 : Working curve for lead

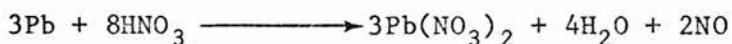
The sample concentrations are found from the working curve and these results are given in table 2.

Table 2 Reaction of lead (0.5g) with 60% aqueous acetic acid (50ml) containing nitre and left to stand for 19 hours

run no.	wt of KNO ₃ added/g	ppm lead	% reaction
11	0.00	75	0.8
12	0.13	166	1.7
13	0.25	242	2.4
14	0.51	313	3.1
15	1.01	344	3.4
16	1.52	406	4.1
17	2.02	469	4.7
18	3.03	555	5.6
19	4.04	688	6.9

The results demonstrate that solubilisation of lead does occur in the presence of nitre, although with increased amounts of nitre, the difference in the amount of lead found in solution is quite small. In a separate experiment addition of potassium chloride to a run the same as run 17 resulted in virtually no lead appearing in solution. This is thought to be due to the formation of an insoluble lead chloride protective coating on the metal.

It is known that dilute, rather than concentrated nitric acid reacts readily with lead.



Therefore, perhaps solubilisation of lead was effected by dilute nitric acid formed from potassium nitrate and acetic acid, contained in the vinegar.

The effect of nitric acid itself was investigated. The results are shown in table 3.

Table 3 Lead turnings (0.5g) added to aqueous nitric acid and allowed to stand for 19 hours

run no.	[HNO ₃]M	ppm lead	% reaction
26	0	1	0
27	0.10	59	0.6
28	0.20	309	3.1
29	0.40	938	9.4
30	0.60	1836	18.4
31	0.80	3203	32.0

The extent of reaction increases noticeably with increasing concentration of nitric acid. The speed with which results are obtained may be attributed to the reaction being a surface one and so the more the piece of lead is cut up, the larger the surface area available to effect reaction. Thus although constancy in surface area was sought, this was difficult to achieve. By comparing runs 19 and 31, which are of the same molarity, the amount of lead found to go into solution is very different. This appears to indicate that reaction with dilute nitric acid in the Chinese recipe cannot be the full explanation.

However it is reported in Mellor,¹⁴ that if the nitric acid used is perfectly free from nitrous acid, it does not attack the lead. Perhaps in the Chinese recipe solubilisation of lead was achieved because of the presence of an impurity in the nitre. We suggest that it is the nitrite ion which is that impurity. The effect of sodium nitrite, which might be present

in naturally occurring nitre⁷⁰ was investigated. The results are shown in table 4.

Table 4 Effect of added nitrite; lead turnings (0.5g) in 60% aqueous acetic acid containing 0.3M nitre with added nitrite

run no.	wt.NaNO ₂ added/g	ppm lead	% reaction
39	0	276	2.8
40	0.035	376	3.8
41	0.069	463	4.6
42	0.138	729	7.3
43	0.207	894	8.9
44	0.276	1294	12.9
45	0.345	1475	14.8

These runs were left to stand for 12 hours before being analysed. By comparing runs 39 and 45, it is seen that the addition of sodium nitrite does markedly affect the amount of lead going into solution. The results also show a trend with ever increasing nitrite concentration demonstrating the effect of concentration of reactants.

These results indicate that the nitrite ion could be the active ingredient which readily brings about the solubilisation of lead.

Finally, the effect of using a more dilute aqueous acetic acid mixture was investigated, the results are tabulated below. Each run was allowed to shake for 2 days.

Table 5 Effect of using 10% aqueous acetic acid mixture,
lead turnings (1.5g) in 10% aqueous acetic acid
containing 0.3M nitre with added nitrite

run no.	wt NaNO ₂ added/g	ppm lead	% reaction
50	0	1750	0.06
54	0.138	24 750	82.5
55	0.207	17 150	57.2
56	0.276	26 350	87.8

Since the amount of lead going into solution was so great, the samples had to be diluted several times before reaching the range of the working curve. This could lead to any small discrepancy in the analysis being magnified when the values are corrected for dilution.

From the results, there is a marked difference in the amount of lead found in solution when nitrite is present, compared to the run when no nitrite is present. Thus, even if Chinese alchemists were not able to obtain more concentrated acetic acid from vinegar, from these results, the reaction rate is still increased by the presence of nitrite ion even in a very dilute aqueous acetic acid mixture.

We conclude that the explanation of the San-shi-liu Shui Fa recipe must be that nitrite was present in the nitre used by the early Chinese alchemists. The exact role which the nitrite plays is unclear and would require further investigation.

To continue, the solubilisation of silver which is described in recipe 30 was then investigated. The same experimental approach was used. The reactants were dissolved in aqueous acetic acid, the silver added and the system left to

shake for a period of time. Again the analysis was performed using atomic absorption spectrophotometry.

The chemistry of this recipe is not so easy to understand. Silver is insoluble in water unless an ingredient such as sodium chloride is present. According to the recipe taken from the San-shi-liu Shui Fa, the silver forms an aqueous solution when placed in vinegar. This experiment was carried out in 60% aqueous acetic acid with the assumption that the Chinese alchemists concentrated the vinegar by the freezing-out technique. This was left for five days and, on analysis, no silver was found to be present in solution. Since the manual is concerned mainly with the solubilisation properties of nitre in vinegar, the recipe most probably involved the addition of nitre. Will the dissolution be effected by dilute nitric acid, formed from potassium nitrate and acetic acid, contained in the vinegar? It is known⁷¹ that silver only reacts with nitric acid in the presence of nitrous acid. The mechanism of such a reaction is not known exactly. A series of experiments was carried out in 60% aqueous acetic acid. The results are displayed in table 6.

Table 6 Reaction of silver with nitre in 60% aqueous acetic acid

run no.	wt of KNO ₃ added/g	time(days)	ppm silver	additives	% reaction
8	4.04	5	< 1	-	0
9	5.05	5	8.5	-	0.4
10	6.06	5	13	-	0.7
12	-	5	-	-	0
16	4.04	2	225	NaNO ₂ (0.02g)	13.8
17	-	2	< 1	HNO ₃	0

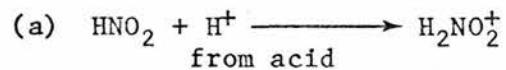
A few problems were encountered during the analysis of the solutions due to the high viscosity of these solutions. Lower concentrations of reactants were used in further experiments. From these results, it can be seen that, no or very little reaction occurred in the presence of nitre and acetic acid. A reaction of silver with nitric acid only also gave no reading. If however sodium nitrite was added a marked increase in the amount of solubilisation was noted. The effect of different concentrations of the nitrite ion species on the rate of reaction was considered, table 7.

Table 7 Silver wire (0.1g) in 60% aqueous acetic acid containing 0.4M nitre with added nitrite

run no.	wt NaNO ₂ added/g	time(hrs)	ppm silver	% reaction
27	0.035	24	4	0.2
47	0.069	24	23	1.1
48	0.138	24	61	3.1
49	0.207	24	93	4.6
32	-	24	0	0

As the concentration of nitrite increased, the rate of reaction also increased. A straight line representation is obtained if a graph of nitrite concentration versus ppm silver in solution is drawn. What role does the presence of nitrite play?

Initially the following hypothesis was considered.



To test whether a reaction of the type (b) would occur, nitrosonium tetrafluoroborate was added to a solution of acetonitrile containing silver wire. The acetonitrile was refluxed over sodium hydride first, to remove any acrylonitrile, followed by refluxing over phosphorus pentoxide to remove any water present, and finally distilled twice to remove any phosphorus pentoxide remaining in solution.

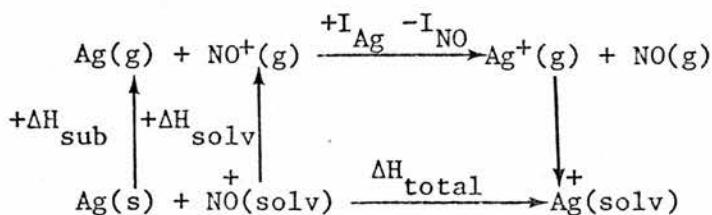
It could be seen that the silver dissolved very readily in the acetonitrile solution containing nitrosonium tetrafluoroborate. In this instance gravimetric analysis was used to determine the percentage of silver in solution. Duplicate samples were taken, the results are shown in table 8.

Table 8 Gravimetric analysis of silver

	wt of precipitate (W)g	wt of silver in 1 litre/g	conc/g ℓ^{-1}
(i)	0.0627	$200 \times W \times 0.7524$	9.435
(ii)	0.0617	$200 \times W \times 0.7524$	9.285

The yield from (i) is 93.83% and (ii) is 92.34%. Therefore silver readily dissolves in the presence of the nitrosonium ion in acetonitrile. The ΔH value found from the following cycle substantiates this.

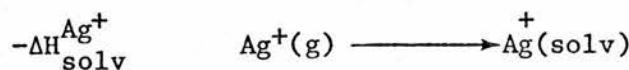
Born-Haber cycle calculation for silver in acetonitrile solution:



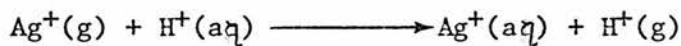
$$\therefore \Delta H_{\text{total}} = \Delta H_{\text{sub}}^{\text{Ag}} + \Delta H_{\text{solv}}^{\text{NO}^+} + I_{\text{Ag}} - I_{\text{NO}} - \Delta H_{\text{solv}}^{\text{Ag}^+} \quad (1)$$

Some of these values are calculated as follows;

$$\begin{aligned} I_{\text{NO}} &= \Delta H_f^\circ(\text{NO}^+) - \Delta H_f^\circ(\text{NO}) \\ &= 987 - 90.7 \\ &= 896.3 \text{ kJ mol}^{-1} \end{aligned}$$

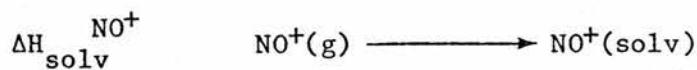


The value quoted by Rosseinsky of 615.6 kJ/g-ion includes the value for a proton



Thus the corrected value for the single ion is

$$-\Delta H_{\text{solv}}^{\text{Ag}^+} = 475.3 \text{ kJ/g-ion}$$



$$\text{Since } \Delta H_{\text{hyd}} \sim \frac{690z^2}{r_{\text{sol}}} \quad (\text{kJ mol}^{-1})$$

$$\text{and } r_{\text{sol}} = r_{\text{therm}} + 0.72^{17}$$

The value r_{therm} of 1.82 for CN^- is used to approximate the r_{therm} value for NO^+

$$\begin{aligned}\text{Therefore } r_{\text{sol}} &= 1.82 + 0.72 \\ &= 2.54\end{aligned}$$

$$\begin{aligned}\text{and so } \Delta H_{\text{solv}}^{\text{NO}^+} &= 690/2.54 \\ &= 271.5 \text{ kJ mol}^{-1}\end{aligned}$$

Substituting these values into equation (1) gives:

$$\begin{aligned}\Delta H_{\text{total}}^{\text{NO}^+} &= +284.1 + 271.5 + 730.89 - 893.2 - 475.3 \\ &= -82 \text{ kJ mol}^{-1}\end{aligned}$$

Although approximations have been made, from this calculation, reaction (b) appears possible. The same calculation was performed for reaction (c) and the following ΔH value found,

$$\Delta H_{\text{total}}^{\text{NO}_2^+} = 105.3 \text{ kJ mol}^{-1}$$

Further experiments were carried out to test the hypothesis proposed on page (111). Silver wire was placed simultaneously into two solutions. One contained nitrosonium tetrafluoroborate in sulpholane, the other nitronium tetrafluoroborate in sulpholane. The rate of solubilisation of silver in the latter was much faster than in the nitrosonium

containing solution. If the proposed mechanism was correct, one would have expected the rate of solubilisation of silver to be faster in the nitrosonium containing solution.

An alternate explanation may be that the nitrosonium species is having a catalytic effect on the reaction. A fresh series of experiments was carried out.

Table 9 Solubilisation of silver (0.1g)

run no.	additives	time(mins)	ppm silver	% reaction
67	NO_2^+ BF_4^- (0.5M) $\text{NO}^+ \text{BF}_4^-$ (0.2M)	60	9272	93
68	NO_2^+ BF_4^- (0.5M) $\text{NO}^+ \text{BF}_4^-$ (0.5M)	30	9 989	~100
69	NO_2^+ BF_4^- (0.5M)	30	8090	81
70	$\text{NO}^+ \text{BF}_4^-$ (0.5M)	30	4900	49

In run 68, the reaction reaches completion, which in this case is total solubilisation of the silver. With a lower concentration of nitrosonium ion, this is attained less rapidly.

Although these results are not sufficient to be conclusive, there are indications that the nitrosonium species may be playing a catalytic role in the reactions here.

In conclusion it can be said that the presence of nitrite as an impurity in the Chinese recipe, does increase the rate of solubilisation of silver. This was found after only 24 hours, therefore after the 30 days mentioned in the San-shi-liu Shui Fa recipe, this effect would be even greater. Whether the effect that the nitrite has can be explained by the presence of the nitrosonium species is questionable. All we can state with certainty, is that the presence of nitrosonium species does result in a higher percentage of reaction being observed (table 9).

In both the recipes taken from the San-shi-liu Shiu Fa, which deal with the solubilisation of silver and lead, the explanation of the chemistry of the processes lies in the presence of sodium nitrite as an impurity in the nitre. The work in this chapter has confirmed the conclusions of Butler et al⁶⁶, that key factors to the success of some of the ancient Chinese alchemical experiments were in fact naturally occurring impurities. A consideration of these impurities which may act catalytically can explain why until recently some of the Chinese alchemical texts have been unfairly dismissed and may also highlight inorganic reactions which have enjoyed little attention.

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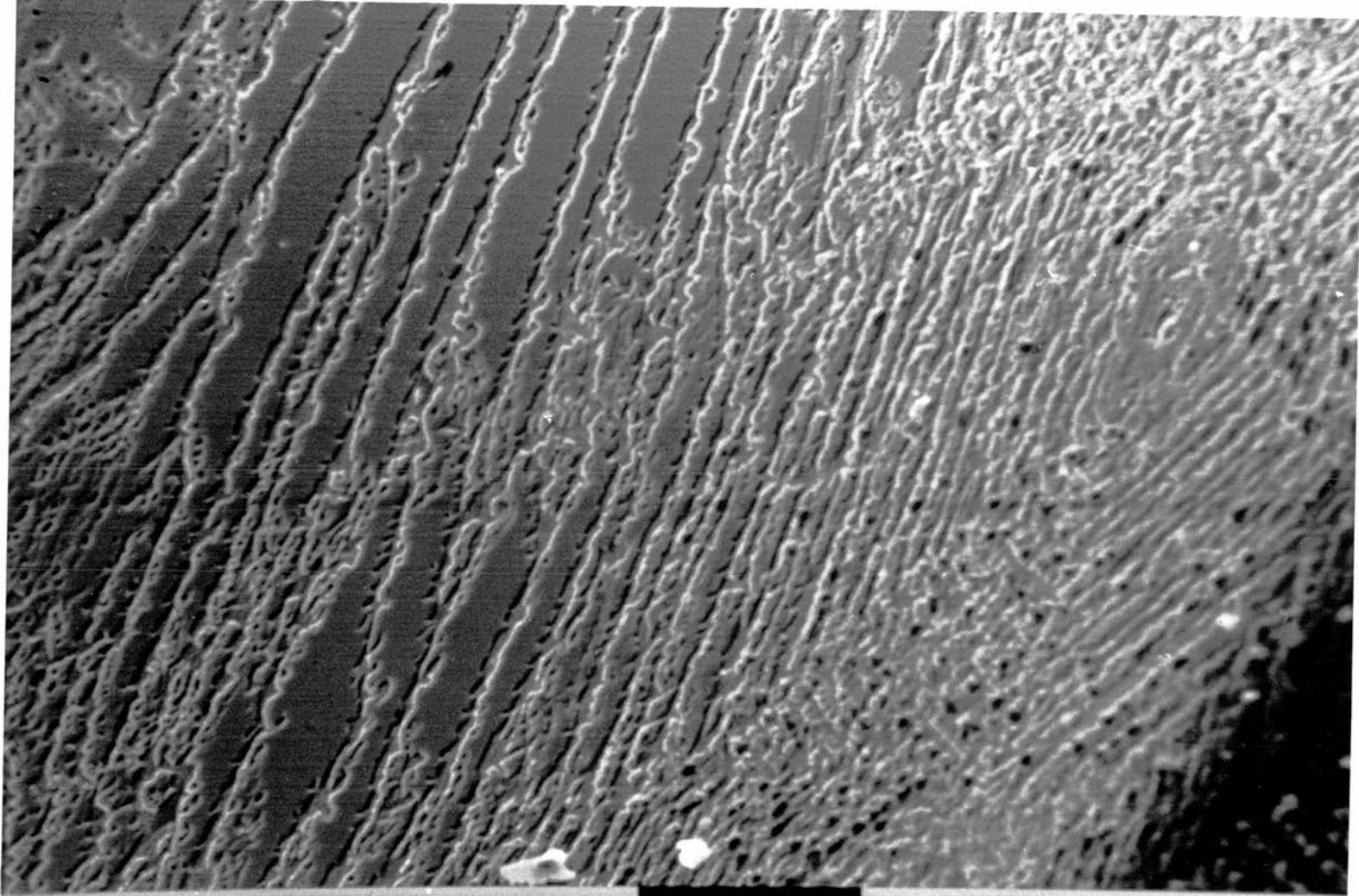
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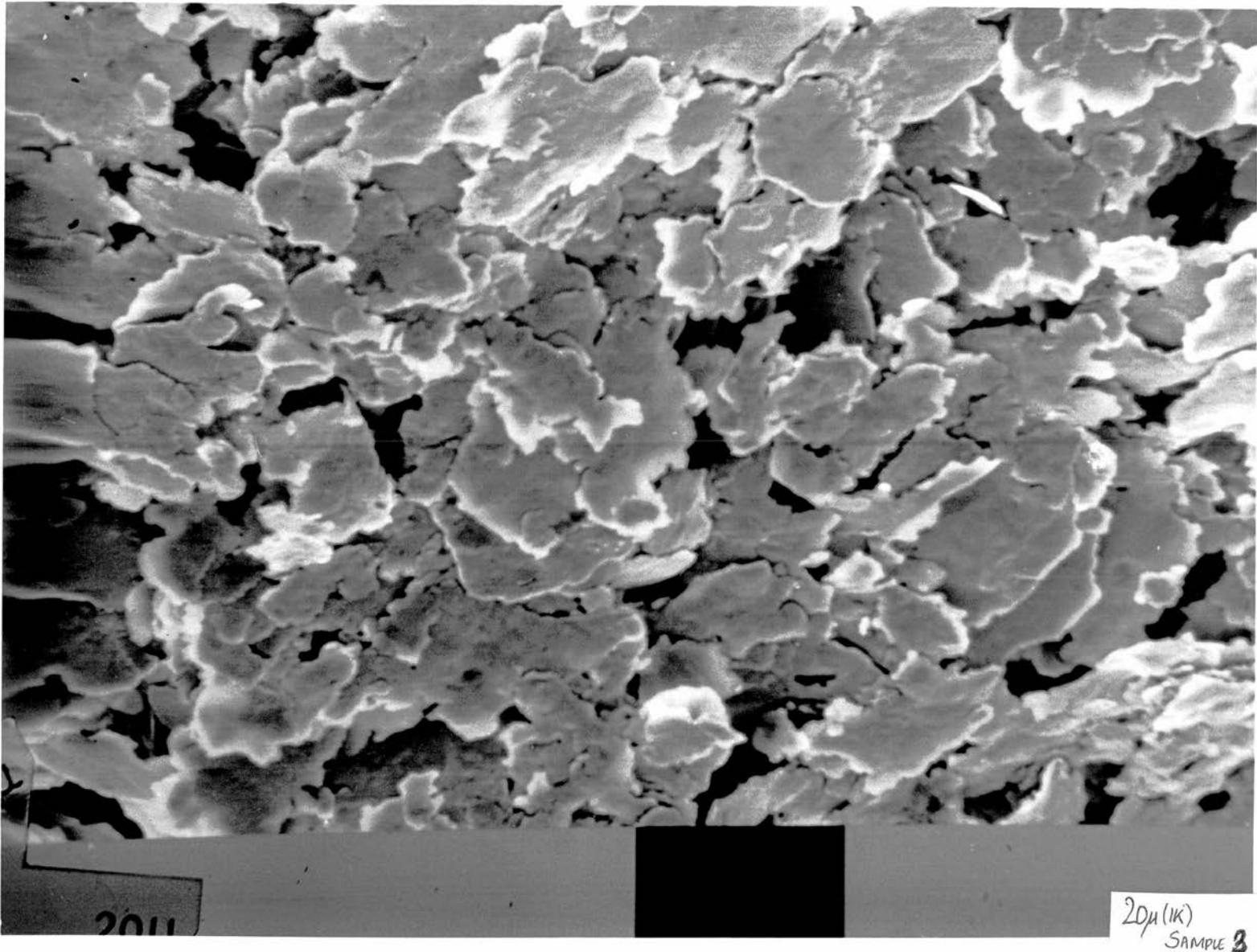
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20μ

20μ SAMPLE 2
ONE PLATELET

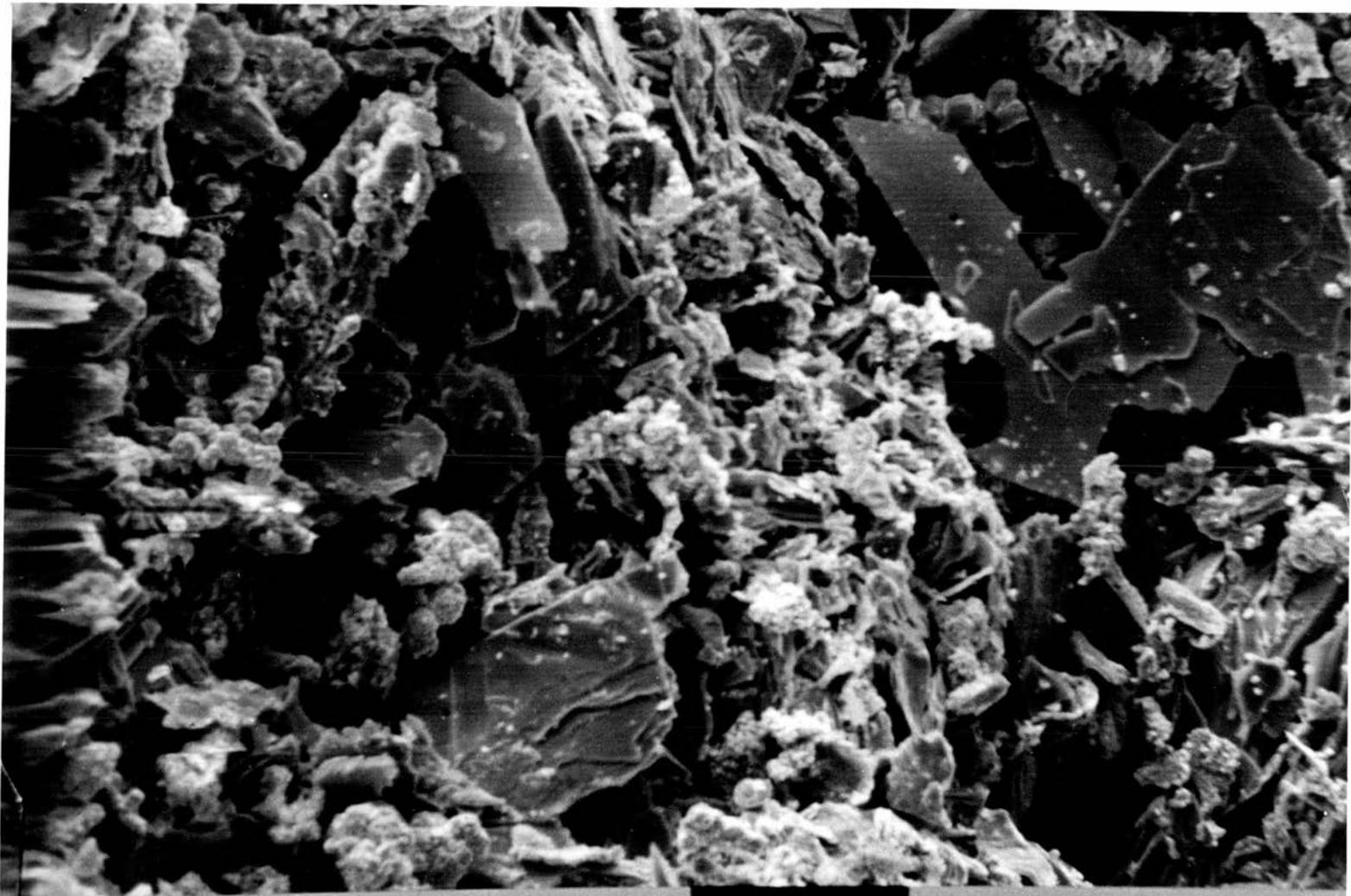
Th
QD18.C5M2



20 μ

20 μ (1K)
SAMPLE 3

Th
QD18.C5M2



40μ

40μ Sample 4

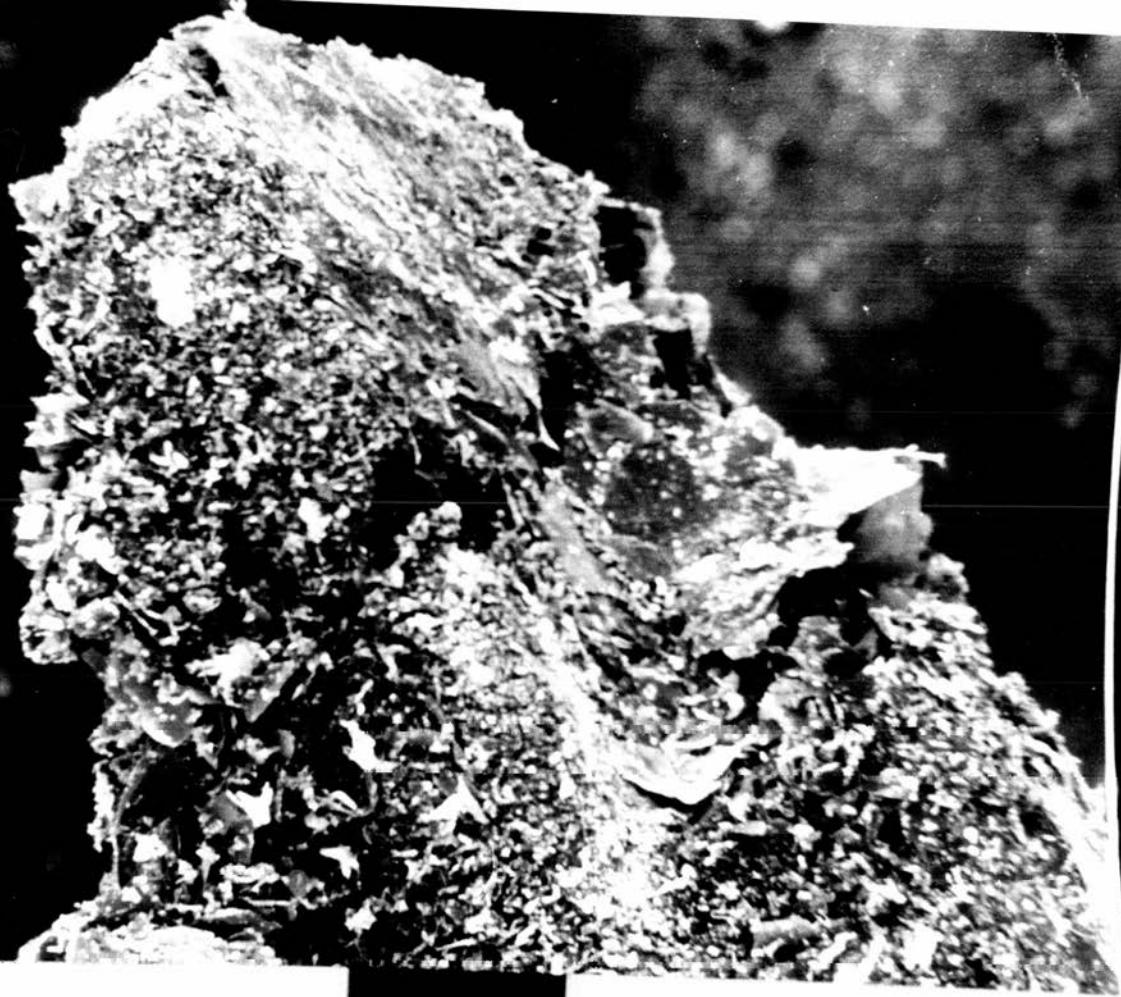
q.
Th
QD 18. C5 M2



100 μ

100 μ SAMPLE 4

Th
QD18.C5M2



400 μ



100 μ SAMPLER

Th

QD18.C5M2



1



2



3



4



5



6



7



8

晋周处墓出土的银制带饰(约原大)(正文127页)

Th
QD18.C5M2

PHOTOGRAPH 1