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REACTIONS OF POTASSIUM THIOCYANATE

AT

HIGH TEMPERATURES

BY

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## ABSTRACT

It was observed that potassium thiocyanate melt shows different colours at high temperatures. The investigations carried out indicate that the colours were due to the formation of colloidal sulfur.

Addition of various metal ions to the melt produced different colours depending on the metal ion added and the temperature of the melt.

At high temperature the sulfur of the potassium thiocyanate melt becomes very active and combines with water to give  $H_2S$ . This reaction because of its sensitivity, can be used to detect structural and crystallization water. A mechanism for this reaction has been proposed which accounts for the various products obtained.

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## INTRODUCTION

When potassium thiocyanate is heated it melts at  $172.5^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$  to a colourless liquid which becomes blue at  $340^{\circ}\text{C}$ . The colour intensity increases to a very dark blue with rise of temperature. On cooling the change in colour is reversible, the light blue colour disappears around  $330^{\circ}\text{C}$  to give the original white potassium thiocyanate solid. If the blue melt is heated above  $500^{\circ}\text{C}$  the melt changes to an opaque red colour. Upon cooling the red colour changes to bluish green and the solid potassium thiocyanate retains a yellow appearance. In 1908 E. Paterno and A. Mazzucchelli<sup>1</sup> observed this blue colour at  $430^{\circ}\text{C}$  and the red colour above  $500^{\circ}\text{C}$ . They ascribed the blue colour to a form of sulfur which they called "blue sulfur". They stated also that there is no appreciable separation of free sulfur in the red melt. Since then, very little work has been done on this interesting phenomenon and most of it was of a speculative nature and inaccurate as far as physical measurements are concerned.

The colour changes obtained on heating and cooling potassium thiocyanate melt could be due to:

- 1) Formation of isomers.
- 2) Formation of free electrons. Such free electrons are considered to be the cause of the blue colour obtained when sodium metal is dissolved in liquid ammonia.



3) Colloidal sulfur, the shape and size of the particles being responsible for the different observed colours.

The objectives of this work were:

a) To determine which of the above factors or possibly which combination of them could satisfactorily explain the observed phenomena.

b) To study the nature of the reaction of the potassium thiocyanate melt with water.

The investigation on the formation of isomers proved to be difficult and inconclusive. The formation of electron holes was briefly investigated but the results were negative. However, all the evidences seemed to be in favour of the formation of colloidal sulfur.

At high temperature the sulfur of the potassium thiocyanate melt becomes very active and combines with water to give  $H_2S$  which can be tested with lead acetate paper. This reaction is extremely sensitive and can be used to detect structural and crystallization water. A mechanism has been proposed which accounts for the various products obtained.

In the first part of this thesis the experiments carried out to determine the nature of the colour of the melt are described. Some additional tests were carried out to investigate the effect of various factors on the coloured

melt. The reactions of the potassium thiocyanate melt with various metal ions were studied qualitatively. A wide range of colours is obtained depending on the metal ion added and the temperature of the melt. It is proposed to relate such reactions with those occurring in nature and which yield coloured semi-precious stones like Lapis Lazuli,  $3(\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2) \cdot 2\text{Na}_2\text{S}$ , and Celestine both of which contain sulfur, while Nepheline ( $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) which does not contain any sulfur is colourless.

The second part of the work consists of a description of the effect of water on the melt of potassium thiocyanate.

## THEORY

### 1. Isomeric structures

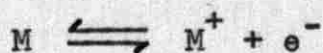
J. Goubeau and O. Gott<sup>2</sup> have shown that thiocyanic acid behaves as a tautomeric mixture of two forms, giving indistinguishable (resonance hybrid) ions,



The alkyl derivatives of the tautomeric forms of thiocyanic acid have been prepared. They are the so-called normal esters,  $\text{R-S-C}\equiv\text{N}$  and the isoesters,  $\text{R-N=C=S}$ . The isothiocyanic esters are more stable and are often formed from their isomers on heating. The stability of the isoesters is increased by resonance. But, no inorganic isomer of the thiocyanate exists. The thiocyanate ion like the cyanate and azide ions is linear<sup>3</sup> and seems to be  $\text{-S-C}\equiv\text{N}$  rather than  $\text{S=C=N-}$ , since the Raman spectrum shows a line assignable to the triple bond, but none for the double  $\text{C=S}$  bond<sup>4</sup>.

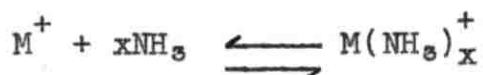
### 2. The electron hole theory

The theory, which is supported by a variety of experimental evidences, of the constitution of alkali metal solutions in liquid ammonia, as proposed by Kraus<sup>5</sup>, assumes the metal atoms to be in equilibrium with metal ions and free electrons,



the ammonia molecules then solvate these ions and electrons

reversibly,



the blue colour being due to the ammoniated electrons.

According to Ogg<sup>6</sup> single electrons and electron pairs that are trapped in cavities which they create in the liquid are responsible for the blue colour of the alkali metals in liquid ammonia. The single electrons and electron pairs are postulated to be in equilibrium with each other, and the equilibrium being influenced by both temperature and concentration. Also, the concept of existence of free electrons may be supported by the work of Laitinen and Nyman<sup>7</sup>.

### 3. Colloidal sulfur

Colloidal sulfur is capable of exhibiting various colours depending on the particle shape and size. Blue colloidal solutions of sulfur were prepared by several methods by various workers. One simple method of preparing, colloidal sulfur is by the addition of sodium thiosulfate to dilute hydrochloric acid.

In colloidal solutions the nature of the dispersing medium<sup>8</sup> will cause the dispersed phase to have a different colour from the colour it has in air. This is due in part to the difference in the index of refraction of the disper-

sing medium and air and in part of the reflecting and absorbing properties of the medium. As an illustration, crystallized copper sulfate which is blue by transmitted light is white when powdered, as a result of scattering by the irregular surface. If this white powder is suspended in an organic liquid which has the same index of refraction, the particles will appear blue.

The interest in colours produced by turbid media arose from the attempts to explain the blue colour of the sky. It was Leonardo da Vinci<sup>9</sup> who first suggested that the atmosphere is in reality a turbid medium. When very fine particles of a substance, which absorbs weakly, are suspended in a transparent solid, liquid or gas these particles scatter blue light more than the red; hence such a system appears red by transmitted light and blue by reflected light. This result has been supported experimentally by the tests of artificial atmospheres of turbid liquids and vapours carried out by Brucke<sup>10</sup>, Roscoe and Tyndall<sup>11</sup>.

The blue of turbid media is known as "Tyndall blue", like for instance, the blue colour of the sky which results from the scattering of light by drops of liquid and particles of dust suspended in the air, or by the oxygen or nitrogen molecules themselves. In blue eyes, where there is no pigment, the colour is a Tyndall blue which is more intense the finer the particles that give rise to the blue colour. Sufficiently coarse particles give grey eyes<sup>8</sup>.

The theory of the Tyndall blue has been worked out by Lord Rayleigh. He showed that for non-conducting spheres the radii of which are small compared with the wave-length of light, the intensity,  $I_s$ , of the scattered light, when the incident light is unpolarized and of intensity  $I_o$ , varies according to the following law<sup>12</sup>:

$$I_s = I_o \frac{(D^1 - D)^2}{D^2} (1 + \cos^2 \beta) \frac{\pi m V^2}{\lambda^4 r^2}$$

where  $D^1$  and  $D$  are the optical densities of the particles and the dispersion media respectively (proportional to the squares of the corresponding indices of refraction),  $m$  is the number of particles per unit volume,  $V$  is the volume of a disturbing particle,  $\lambda$  is the wave-length of the scattered light,  $\beta$  is the angle between the line of sight and the incident light, and  $r$  is the distance of particles from the observer.

Polarization of light at right angle to the incident beam is a property of colloidal solutions. Barnes and LaMer<sup>13</sup> showed that sulfur sols of very small particle size polarize light at  $90^\circ$  to the direction of the incident beam.

The colour of a colloidal solution depends on the dimensions of their particles. Faraday<sup>14</sup> proved that gold colloidal solutions containing the smallest particles of gold have red or ruby tints by transmitted light, while if,



for any reason, the particles become larger and larger, the colour by transmitted light tends more and more to the blue.

Ostwald rule<sup>15</sup> states that the variation in colour of sols with particle size is due to a shifting of the absorption maximum towards the regions of longer wavelength with decreasing degree of dispersion. If this rule applies, the colour of a given sol would change through yellow → red → blue → purple → green with increasing particle size. This appears to occur with sols of sulfur and selenium, but the rule is not generally applicable to metallic sols.

The colour is also affected by the shape of the particles which may be spherical or not. According to Mie<sup>16</sup> red gold sols consist of spherical particles under 40 m $\mu$  in radius, whereas blue gold sols have larger particles. Yet blue gold sols have been prepared in which the particles are much smaller than 40 m $\mu$ . This is explained by assuming either that the particles are not spherical or that they consist of loose aggregates of smaller units. Therefore, the colour of a given sol is a complex resultant light effect which depends: on the nature of the dispersed phase and of the dispersion medium; on the size and shape of the primary particles and on the form and closeness of their packing in agglomerates.

## EXPERIMENTAL

### Part I

The potassium thiocyanate Merck reagent was dried for two hours at 110 - 120°C. before use. The chemical composition is:

a) Insoluble ingredients	max. 0.005%
b) Insoluble ingredients in alcohol	max. 0.005%
c) Chloride (Cl)	0.005%
d) Sulfate (SO <sub>4</sub> )	0.001%
e) Sulfide (S)	0.001%
f) Heavy metals (Pb)	0.0008%
g) Iron	0.0001%
h) Ammonium (NH <sub>4</sub> )	0.001%
i) Sodium (Na)	0.02%

Dried crystals of potassium thiocyanate were placed in a pyrex tube and heated to the melting point. Heating was provided either by a Bunsen flame or by winding a nickel-chrome wire around the test tube coated with asbestos paste. A slit was left to observe variations in colour. Temperature measurements were made with a chromel-alumel thermocouple which was calibrated at the boiling point of distilled water, naphthalene, benzophenone and sulfur. The cold junction was dipping in crushed ice.

The following table shows the variation in the colours of potassium thiocyanate melt at different temperatures.



Table 1

Variation of Colour at Different Temperatures

KSCN MELT	
Colour	Temperature °C.
Colourless	below 310
Very pale gold colour	at 317
Light blue appears	at 340
Blue	at 393
Deep blue	at 444
Red	above 500

When the melt is cooled from 350°C the colour changes from blue to colourless around the transition point i.e. 340°C. When cooling is done from 400°C and 460°C the transition point is difficult to determine accurately because the melt maintains a yellow colouration. Upon cooling the red melt turns to deep blue → greenish blue → oily green → brown liquid which solidifies into an orange yellow solid.

The same experiments were repeated with  $\text{NH}_4\text{SCN}$  (M.P. 149.6°C) but no blue colour was observed. It seems the decomposition of the  $\text{NH}_4^+$  causes a breakdown of the

structure responsible for the blue colour. The physical constants of related compounds are shown in Table 2.

Table 2  
Physical Constants

Compound	Melting point °C	Boiling point °C	Molecular weight
NH <sub>4</sub> SCN	149.6	d. 170	76.12
KSCN	173.2	d. 500	97.18
KCN	634.5; (601-621)		65.11
KOCN	d. 700-900		81.11

When a drop of water is added to the colourless KSCN melt it develops a sizzling oily appearance and is rapidly changed to steam. When the melt is blue and a drop of water is added a strong odour of H<sub>2</sub>S is detected. If a crystal of a hydrated salt is added to the melt H<sub>2</sub>S is formed; if however, the same salt is added in its anhydrous form no H<sub>2</sub>S is generated.

A.- Detection of isomeric structures

The Beckman Spectrophotometer Model DU could not be used for absorption measurement of the blue melt because of the difficulties which arose in heating the Beckman cell.

The solid KSCN was heated in a test tube around which a nickel-chrome wire was wound. The terminals of the wire were connected to the source through a powerstat transformer to regulate the voltage. When the test tube was introduced in the chamber of the cell holder and heated no absorption measurements could be made because the infrared radiations from the hot test tube affected the phototube. Unless the cell holder and the cell are modified to accommodate a system working at high temperature the Model DU cannot be used for that purpose.

#### B.- Electron magnetic resonance

Professor Frans Bruin (Physics Department, American University of Beirut) tried to observe the magnetic resonance absorption of the colourless, blue and red melts of potassium thiocyanate at 60 mc/s in the field of Helmholtz coils of about 20 gauss. The results were negative; but this however does not imply that free electrons are absent since the sensitivity at such a frequency is very low.

#### C.- Experimental evidences in favour of colloidal sulfur

1. Tyndall Effect: A white beam of light was directed through a slit from a 6 volt tungsten lamp at the blue melt maintained at 350°C in a test tube. A strong Tyndall effect is observed as shown in Fig. 1. The scattered light was found to be polarized at right angle to the incident beam when viewed through a polaroid filter. The colourless melt maintained at a temperature just above the melting point of

KSCN does not show a similar Tyndall effect as shown in Fig. 2.



Fig. 1  
Tyndall effect in the KSCN melt at 350°C.



Fig. 2  
Absence of Tyndall effect in the KSCN melt at a temperature  
Just above the melting point of KSCN

2. Tyndall Blue: It was observed that with rise of temperature the light blue colour of KSCN melt became darker blue. As the temperature rises, more KSCN decomposes. Sulfur particles in larger number and smaller size are liberated causing a deepening in the blue colour.

3. Particle Size: When the colourless melt is heated to  $350^{\circ}\text{C}$  and cooled the blue colour appears and disappears in a reversible way, and the solid obtained is white. If the blue melt was cooled from  $400^{\circ}\text{C}$  the colour changes around  $300^{\circ}\text{C}$  to a faint dirty green; and when the liquid solidifies the solid does not have a pure white colour. When the opaque deep blue melt is cooled from  $460^{\circ}\text{C}$  the blue changes to a greenish blue colour between  $250 - 300^{\circ}\text{C}$  and the liquid solidifies to a yellow solid. Heating the blue melt above  $500^{\circ}\text{C}$  gives an opaque red liquid which on cooling turns deep blue  $\longrightarrow$  greenish blue  $\longrightarrow$  oily green  $\longrightarrow$  brown liquid, which solidifies into an orange yellow solid.

According to Ostwald<sup>15</sup> rule the variation of colour in the melt of KSCN is partly due to variation in size of the colloidal particles. The size of the particles in the brown melt is larger than those in the green melt. Those in the green melt are larger than those in the blue melt; and those in the blue melt are larger than those in the red melt. Thus the size of the colloidal particles, which are formed by heating, decreases with rise of temperature and increases on cooling; which is in agreement with the above mentioned rule.

4. Absorption Spectrum: In order to investigate the absorption spectrum of the blue melt a Hilger Quartz

Spectrograph was used. The absorption spectrum of the blue melt was compared with a blue colloidal solution of sulfur of practically the same colour and intensity. A blue solution of sulfur in fuming sulfuric acid (65%  $\text{SO}_3$ ) was prepared and its absorption spectrum was taken in the visible region (8000 - 3200  $\text{\AA}$ ). A fresh solution has to be used because the blue colour fades with time. A tungsten light source was used at 34.5 cm from the slit. A condensing quartz lens (F 958) was placed 28 cm from the slit. The sample was at a distance of 2 cm from the slit. The slit width was 0.005 mm and the exposure time was 2.5 minutes. The blank was the fuming sulfuric acid. The absorption spectrum of the blue melt at 354°C was done under similar conditions as above, but with a slit width 0.01 mm and an exposure time of 3 minutes. The blank was the colourless melt at 240°C. The plates were developed with an ID-2 developer for 4 minutes, rinsed with water for 10 seconds, fixed in IF-15 fixer for 15 minutes, and washed with water for 25 minutes. The temperature of all solutions and water was kept at 20°C. They were then scanned with a densitometer comparator (SER. NO. CBI-67, Baird Associates, Inc.,) which plotted the optical density versus distance. The relative units of distance were converted to wave-length units from a calibration curve. Fig., 3 shows that the absorption curve of the melt has two peaks with a maximum absorption at 587.0  $\mu$  and 642.5  $\mu$ . The absorption curve

of the sulfur solution is similar to the absorption curve of the melt, and it also shows two peaks at 580.0  $\mu$  and 644.3  $\mu$  as shown in Fig. 4.

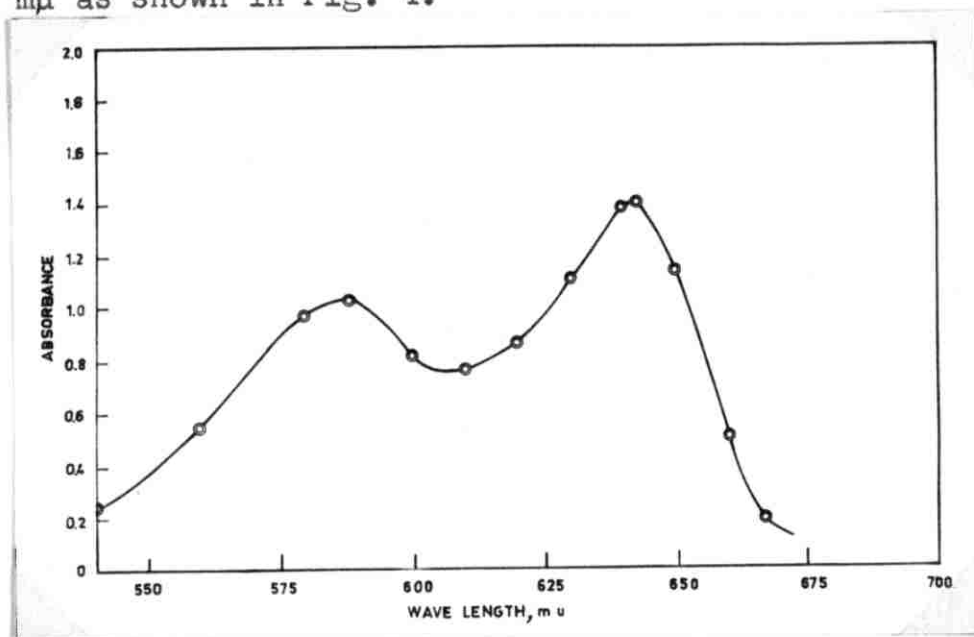


Fig. 3  
Visible Absorption Spectrum of KSCN Melt at 354°C.

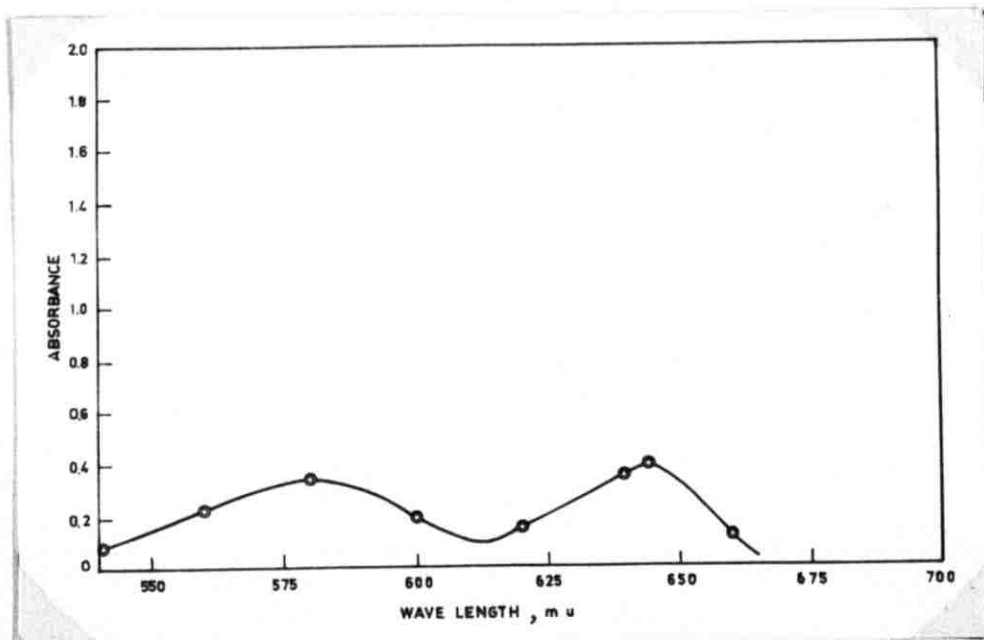


Fig. 4  
Visible Absorption Spectrum of Sulfur in Fuming Sulfuric Acid at Room Temperature.

5. Black copper sulfide was formed when a piece of copper metal was immersed in the blue melt of KSCN. When the copper metal was immersed in the colourless melt no black colour was observed. This indicates that the formation of blue colour in the melt is associated with the liberation of sulfur from the KSCN. A brief description is given later on the effect of different metallic ions in the KSCN melt.

6. Reaction of the blue melt with water (see Part II)

D.- Additional tests

1. Effect of reducing the pressure on colour. When KSCN was heated under a low pressure of 2-6 mm of mercury, the blue colour appeared, changing to very dark blue near the appearance of the red colour. The red colour was not observed on continuous heating and yellow sulfur was deposited near the mouth of the test tube.

2. Heating KSCN in a test tube to the blue colour between 370 - 400°C. for 30 hours or more did not change the nature of the blue colour. It was also observed that yellow sulfur distilled over and condensed on the upper part of the test tube, while the melt remained bluish all the time.

3. Heating solid KCN and sulfur produced an intense red colour in their melt, while the blue colour appeared on the sides of the test tube. On cooling the solid was yellow. Its solution gave a red colour with ferric ions,



showing that some thiocyanate was formed.

4. Effect of bubbling nitrogen, hydrogen, oxygen and air through the melt of KSCN. Bubbling pure dry nitrogen gas into the blue melt has no effect on the formation of the blue colour; except that sulfur is carried out of the melt and deposited near the mouth of the test tube.

When dry hydrogen gas was bubbled no smell of  $H_2S$  could be detected. Continuous bubbling of hydrogen produces the same effect as bubbling nitrogen gas.

Bubbling oxygen did not affect the colour formation; but  $SO_2$  gas evolved and some sulfur deposited near the mouth of the test tube. When ferric ions were added to the water solution of the solidified melt a green colour was obtained.

The bubbling of air produced the same effect as bubbling oxygen, except that addition of ferric ions to the solution of the solidified melt produced a black precipitate.

Whenever different gases were passed through the melt, the bubbling caused a cooling effect which reduced the intensity of the blue colour. On cooling while bubbling the solid obtained was colourless because the sulfur which was decomposed from potassium thiocyanate was carried out. Some of the sulfur condensed, but when air or oxygen was used the sulfur was oxidized and escaped as  $SO_2$ .

The yellow substance condensing near the mouth of the test tube, in all the above additional tests, gave a positive

test for sulfur by conversion to thiocyanate<sup>1</sup>.

5. Addition of metallic ions to KSCN melt. The presence of free active sulfur particles in the melt of KSCN leads to some very interesting colour effects when metallic ions are added. The colours which are obtained are not normally those of the corresponding sulfides. It was noted that the colour changed as the temperature increased suggesting a variation in the size of the sulfur particles. Upon quenching and sudden chilling, the solid retained the colour of the melt when hot with very slight changes in the intensity of the colour. It is tempting to associate this phenomenon with those occurring in nature whereby melts containing colloidal sulfur are subjected to tremendous pressure and high temperature and give upon cooling coloured crystals. It has been proved that the blue colour of the semi-precious ultramarine is due to the presence of colloidal sulfur<sup>17</sup>.

Since different colours are obtained at different temperatures it is conceivable that the same mixture can yield different coloured crystals depending on the temperature of the melt.

The following is a very brief investigation on the addition of metallic ions to the KSCN melt.

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<sup>1</sup> See Appendix for the details of this test.

<u>Ions added</u>	<u>Colours Observed</u>
Co <sup>++</sup>	Violet which changed to blue upon increasing the temperature.
Cd <sup>++</sup>	Yellow at low temperature. Changed to orange and then red with rise of temperature.
Sb <sup>+++</sup>	Yellow changing to dark green and then black.
Fe <sup>+++</sup>	Difficult to observe because the colour changes were masked by the deep red colour of ferric thiocyanate.
Al <sup>+++</sup>	A white froth is obtained. Yellow sulfur formed at the surface.
Cr <sup>+++</sup>	Green.
Bi <sup>+++</sup>	Red changing to brown to black.
As <sup>+++++</sup>	Yellow changing to orange to red.

With Sn<sup>++</sup> no appreciable change was obtained while with Cu<sup>++</sup> sulfur was formed and distilled onto the sides of the tube.

Part II

When potassium thiocyanate is fused to about 340°C. it turns blue. The colour disappears when the melt is cooled. This is probably due to the splitting off of sulfur, which remains in highly dispersed colloidal form in the molten KSCN and which reforms KSCN on cooling.



The sulfur which is obtained in the blue melt is highly reactive and displays reactions which are not realizable in aqueous solutions of KSCN, such as the formation of CuS and Ag<sub>2</sub>S from metallic copper and silver; and the liberation of H<sub>2</sub>S when water or inorganic materials which liberate water at high temperatures are added to the KSCN melt<sup>18</sup>. Since the H<sub>2</sub>S which is liberated is readily detected by lead acetate paper, it becomes possible to detect adsorptive or chemically bound water.

While analyzing the nature of the gases that are evolved upon the addition of water it appeared that the problem was complex because of the simultaneous formation of SO<sub>2</sub>, NH<sub>3</sub> and CO<sub>2</sub>. The analysis of such a mixture in presence of H<sub>2</sub>S proved to be difficult.

For this series of experiments the dried solid KSCN

is put in a flask connected to a separatory funnel and a delivery capillary tube dipping into distilled water in which the gases are collected. Water is introduced when the melt becomes blue. It was observed that the minimum temperature at which  $H_2S$  is formed was around  $250^{\circ}C$ . Experimental details of the tests are given in the Appendix.

#### A.- Analysis of the gaseous products

1. Detection of  $H_2S$ :  $H_2S$  is liberated when water or a compound containing water is added to the blue melt of  $KSCN$ . The  $H_2S$  is easily detected by its smell and its action on filter paper moistened with a 10% lead acetate solution. The intensity of the black speck developed is an indication of the quantity of  $H_2S$  liberated.

2. Detection of  $NH_3$ : Ammonia was determined directly from the solution in which the gases were collected after eliminating  $H_2S$  by the addition of saturated  $HgCl_2$  solution. Excess dilute  $NaOH$  was then added and the solution boiled. The gas liberated turned red litmus paper blue and formed a brown red precipitate in the clear drop of Nessler's solution on the knob of a glass rod.

3. Detection of  $CO_2$ : The above solution from which the ammonia has been driven off by boiling was oxidized with 30%  $H_2O_2$  to change the sulfides and any sulfite, which interfere in the sodium carbonate-phenolphthalein<sup>1</sup> test, to

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<sup>1</sup> See Appendix for the details of this test.

sulfate. Then addition of 2N H<sub>2</sub>SO<sub>4</sub> liberated a gas which decolourized the drop of the sodium carbonate-phenolphthalein reagent. This indicates the presence of CO<sub>2</sub> gas.

4. Detection of SO<sub>2</sub>: The identification of SO<sub>2</sub> was made by three different tests:

- a. The zinc nitroprusside test<sup>1</sup>.
- b. The nickelous hydroxide test<sup>1</sup>.
- c. Polarography.

a) Hydrogen sulfide which interferes with the zinc nitroprusside test for SO<sub>2</sub> was removed by adding saturated HgCl<sub>2</sub> solution to a fresh portion of the solution in which the gases were collected. After centrifugation, addition of 2N H<sub>2</sub>SO<sub>4</sub> to the centrifugate liberated a gas which changed the salmon colour of Zn [Fe(CN)<sub>5</sub>NO] precipitate to deep red.

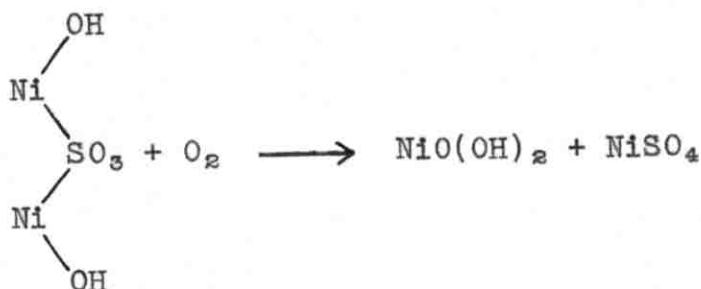
b) In the nickelous hydroxide test, the auto-oxidation of SO<sub>2</sub> induces the oxidation of the green nickelous hydroxide to the black nickelic (IV) hydroxide.

A probable explanation of this effect is that the initial product, basic nickel sulfite, on contact with air is oxidized both cationically and anionically.



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<sup>1</sup> See Appendix for the details of this test.



The oxidation of  $\text{Ni(OH)}_2$  by  $\text{SO}_2$  and atmospheric oxygen may therefore be used as a test for  $\text{SO}_2$ . The colour change is quite distinct but for very small amounts of  $\text{SO}_2$  use is made of the conversion of benzidine acetate to "benzidine blue" by the nickelic hydroxide.

Addition of 6N HCl to the centrifugate obtained in the previous test liberated a gas which changed the green nickel (II) hydroxide on a filter paper to the black nickel (IV) hydroxide. Upon addition of a drop of benzidine acetate the colour turned blue.

c) According to Kolthoff and Miller<sup>19</sup> sulfurous acid gives a half-wave potential of -0.38 volts at the dropping mercury electrode versus the saturated calomel electrode. A fresh portion of the gaseous solution, which was made 0.1N with  $\text{HNO}_3$ , showed a decomposition potential of -0.333 volts and a half-wave potential of -0.38 volts versus a saturated calomel electrode. A known solution of  $\text{SO}_2$  in water, which was freshly prepared by the action of concentrated sulfuric acid on copper metal and which was made 0.1N with  $\text{HNO}_3$ , showed the same decomposition potential and half-wave potential.

### B.- Analysis of the solid residue

The following tests were carried out on the residue of the KSCN melt to which water had been added. On cooling, the residue in the flask retained a yellow colour suggesting that free sulfur is formed.

1. Detection of  $\text{SCN}^-$  and  $\text{S}^{2-}$ : A part of the residue was extracted with water. Addition of a drop of the extract to a drop of ferric ions gave a red colour and a black precipitate. Adding excess of the water extract to a drop of ferric ions gave a black precipitate of iron sulfide, while adding excess ferric ions to one drop of the extract gave a red colour of ferric thiocyanate. The former result shows the presence of sulfide ions and the latter shows that thiocyanate ions are present either unreacted or are formed by the reaction of KCN and sulfur.

2. Detection of  $\text{CN}^-$ : The sulfides from the water extract were removed by the addition of saturated  $\text{HgCl}_2$  solution and centrifugation. A  $\text{CuS}$  precipitate freshly prepared was dissolved in the centrifugate by forming the soluble cuprocyanide complex<sup>20</sup>  $[\text{Cu}(\text{CN})_3]^-$ . This shows the presence of cyanide ions.

3. Detection of free sulfur: The presence of free sulfur in the residue was confirmed by the formation of thallium polysulfide<sup>1</sup>.

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<sup>1</sup> See Appendix for the details of this test.



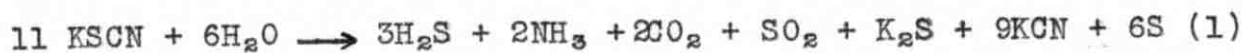
conversion to thiocyanate<sup>1</sup> could not be used in this instance because of the presence of thiocyanate in the solid residue.

When black thallos sulfide, finely dispersed in the capillaries of filter paper, comes in contact with a solution of sulfur, a red brown polysulfide ( $2Tl_2S.Tl_2S_3$ ) is rapidly formed. The polysulfide differs from the  $Tl_2S$  not only in colour but also in its chemical properties. Whereas  $Tl_2S$  dissolves directly in mineral acids the polysulfide is not attacked. Therefore, if black thallos sulfide paper is spotted with a drop of solution of sulfur, in a colourless solvent, and then bathed in a solution of mineral acid a red brown stain still remain where the drop was applied.

A drop of the extract obtained from treating the residue with carbon disulfide gave a positive test for free sulfur while the carbon disulfide alone failed to do so.

### C.- Overall mechanism

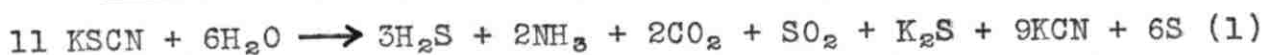
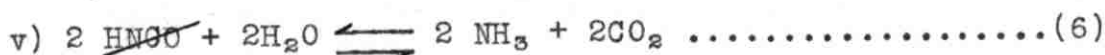
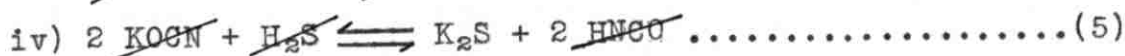
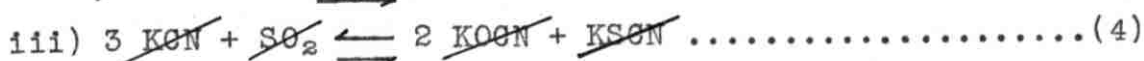
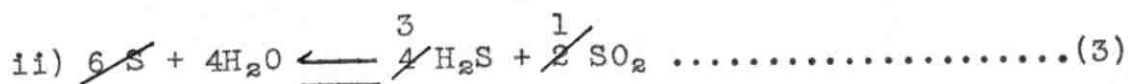
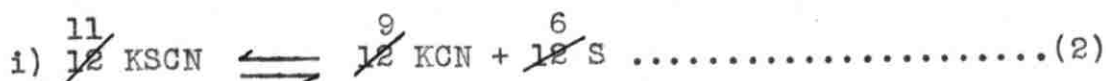
The equation for the net reaction of KSCN with water taking into account the various products would be:



A possible mechanism for the reaction may take place in five main steps which add up to give equation (1).

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<sup>1</sup> See Appendix for the details of this test.



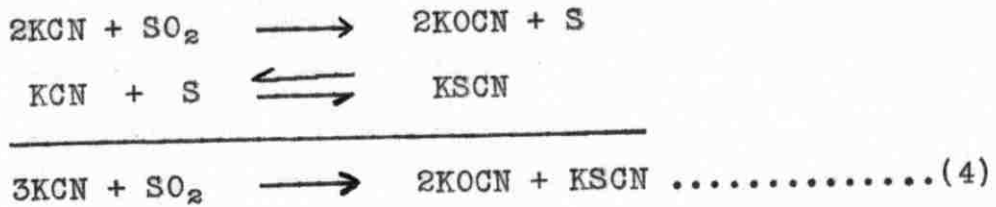
The following is a discussion of the above reactions and a justification of their validity.

Step i. Upon heating, KSCN decomposes to give KCN and free sulfur which condenses near the mouth of the container. When the red or the deep blue melt of KSCN is chilled or quenched quickly in  $\text{CCl}_4$  containing solid  $\text{CO}_2$  it gave an orange-yellow solid. The pyridine extract of this solid gave a positive thallium polysulfide test showing the presence of free sulfur, while the water solution of the solid gave a positive test for cyanide ions with the copper sulfide test.

Step ii. This reaction  $3\text{S} + 2\text{H}_2\text{O} \rightleftharpoons \text{SO}_2 + 2\text{H}_2\text{S}$  was observed by many workers. C.F. Cross and A.F. Higgin<sup>21</sup> found that sulfur decomposes water around  $95^\circ\text{C}$  producing a trace of  $\text{H}_2\text{S}$  and  $\text{SO}_2$ . G. N. Lewis and M. Randall<sup>22</sup> determined the equilibrium constant for this system at the boiling point of sulfur.  $K_{\text{eq}}$  equals 0.00088 to 0.00232. E. Mulder<sup>23</sup> showed that above  $400^\circ\text{C}$  both gases,  $\text{SO}_2$  and  $\text{H}_2\text{S}$ , can exist

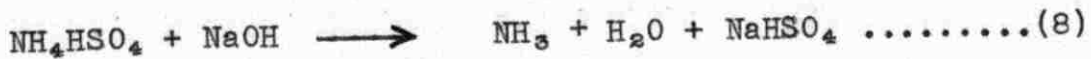
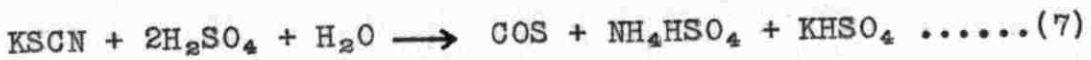
together in the presence of steam. The value of the equilibrium constant for the reaction at  $444.6^{\circ}\text{C}$ , the boiling point of sulfur, indicates that appreciable amounts of  $\text{SO}_2$  and  $\text{H}_2\text{S}$  are formed. As these gases are being continuously removed from the reaction, the equilibrium will be shifted to the right.

Step iii. The experimental evidence for this step was made in the following way.  $\text{SO}_2$  gas, generated from the reduction of concentrated sulfuric acid with metallic copper, was bubbled through the colourless melt of KCN in a test tube. The colour of the melt changed to yellow, to brownish red and then to blue. Upon cooling the solid may be yellow or colourless depending upon whether free sulfur is present or not. The sulfur may come either from the reduction of  $\text{SO}_2$  during the formation of KCN or from the decomposition of KSCN formed during the reaction. Some free sulfur may deposit on the sides of the test tube because it is being carried out of the melt when excess  $\text{SO}_2$  is bubbled through. The equation for the reaction is represented thus:

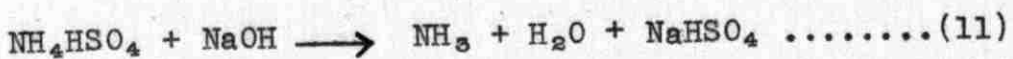
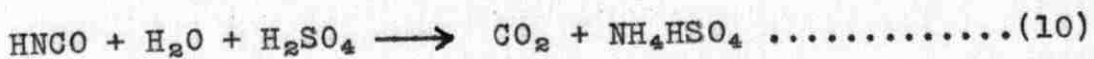
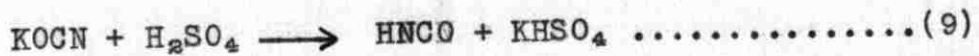


The solidified melt was dissolved in water for analysis. The copper sulfide test for cyanide ions was negative, showing that the cyanide ions reacted completely. The test for thiocyanate ions in the presence of cyanate ions presents no difficulty, whereas the detection of cyanate in the presence of thiocyanate is complex. When one drop of the solution was added to one drop of ferric ions a red colour appeared indicating the formation of thiocyanate ions. To confirm the presence of cyanate ions the following tests were carried out.

The reaction of KSCN solution with dilute sulfuric acid gives no effervescent  $\text{CO}_2$  in the cold, but on boiling a yellow solution is formed. See equation (7).



The reaction of KOCN solution with dilute sulfuric acid gives effervescent  $\text{CO}_2$  in the cold, and on boiling the solution remains colourless. See equations (9) and (10).

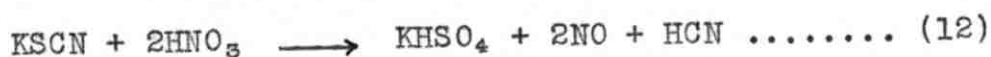


Addition of dilute NaOH will liberate ammonia from

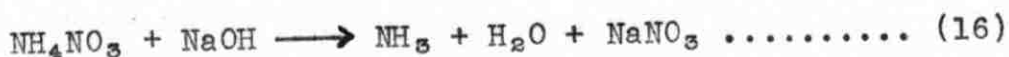
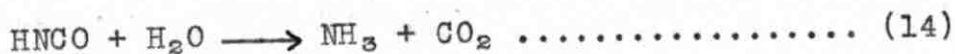
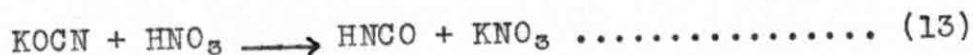
each of the above solutions, as shown by equations (8) and (11).

A known mixture of KSCN and KOCN with dilute  $H_2SO_4$  gives effervescent  $CO_2$  in the cold due to the presence of KOCN. The solution of the solidified melt with dilute  $H_2SO_4$  gave effervescent  $CO_2$  in the cold. Therefore, this shows the presence of cyanate ions. Addition of dilute NaOH to the acid solution liberated ammonia which was tested by Nessler's reagent. The  $CO_2$  gas was tested with the sodium carbonate-phenolphthalein test.

The reaction of KSCN solution with dilute  $HNO_3$  gives a very light brown coloured solution with no effervescence in the cold. Upon little warming a red colouration is produced with the evolution of nitric oxide and hydrogen cyanide gases. It is seen from equation (12) that neither  $CO_2$  nor ammonia is produced from thiocyanate.



The reaction of KOCN solution with dilute  $HNO_3$  gives effervescent  $CO_2$  in the cold. When this acid solution is made alkaline with NaOH it liberates ammonia. This is shown in equations (13) to (16).

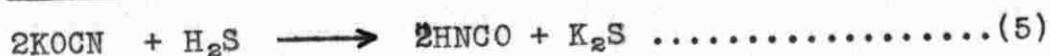
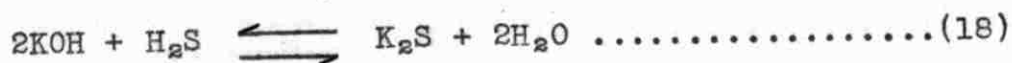


A known mixture of KSCN and KOCN with dilute  $HNO_3$

gave effervescent  $\text{CO}_2$  in the cold due to the cyanate ions, with a light brown colouration due to the thiocyanate ions. When this solution was made alkaline with  $\text{NaOH}$ , ammonia gas was evolved. The solution of the solidified melt with dilute  $\text{HNO}_3$  gave also effervescent  $\text{CO}_2$  in the cold and a light brown colour. When this acid solution was rendered alkaline with  $\text{NaOH}$ , the gas that evolved gave a positive Nessler's test showing the presence of ammonia also.

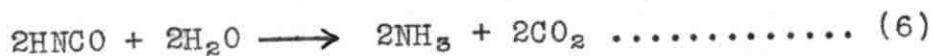
Thus the evolution of  $\text{CO}_2$  in the cold with dilute  $\text{H}_2\text{SO}_4$  and dilute  $\text{HNO}_3$ , and of ammonia from the solution to which dilute  $\text{HNO}_3$  has been added shows the presence of cyanate ions in the solution of the solidified melt.

Step iv. Potassium cyanate hydrolyzes <sup>24</sup> in aqueous solution without addition of a cid, but it is relatively stable in a strongly basic solution. The reactions in this step are represented by equations (17) and (18).



The moment  $\text{HNCO}$  is formed it is decomposed according to step v into  $\text{NH}_3$  and  $\text{CO}_2$ . This will shift the equilibrium of equation (17) to the right. The  $\text{KOH}$  which is left absorbs  $\text{H}_2\text{S}$  as shown in equation (18) and the net result gives equation (5) which is step iv.

Step v. The cyanate ion, identical with the isocyanate, is isoelectronic with  $\text{CO}_2$  and the azide ion ( $\text{N}_3^-$ ) and, like these bodies, is greatly stabilized by mesomerism of the forms  $\text{N}\equiv\text{C}-\text{O}-$  and  $-\text{N}=\text{C}=\text{O}^{25}$ . Isocyanic acid,  $\text{H}-\text{N}=\text{C}=\text{O}$ , rapidly hydrolyzes to  $\text{NH}_3$  and  $\text{CO}_2$  at room temperature while cyanic acid polymerizes to the trimeric cyanuric acid. The acid formed at high temperature in step iv is probably isocyanic acid,  $\text{HNCO}$ , the hydrolysis product of which is  $\text{NH}_3$  and  $\text{CO}_2$  as it is represented by the well known equation (6).



## CONCLUSION

The investigation carried out and described in this thesis indicates that the colour changes which are observed when KSCN is heated are due to the formation of colloidal sulfur. The different colours can be explained by the different sulfur particle size at different temperatures. The variation in colour is in line with the expected change based on particle size.

Experimental evidence is very much in favour of the colloidal phenomenon. Thus the strong Tyndall effect, the absorption spectrum of the blue melt, the formation of free sulfur and its high reactivity with  $H_2O$  indicate the presence of colloidal sulfur. KSCN melt shows a marked activity which is not shown by solutions of KSCN. The presence of colloidal sulfur will lead to the formation of a large number of very small particles which would account for their high activity; thus when water is added to the melt  $H_2S$  is generated.

This is accompanied by a series of side reactions leading to the formation of a number of gaseous products which have been identified.

The change in colour of the KSCN melt could also be due to the formation of isomers; this seems unlikely however in view of the gradual change in colour and the



large variety of colours obtained. The fact that no inorganic isomers of thiocyanates have been obtained could be of significance had it not been for the unusual conditions under which the KSCN is studied.

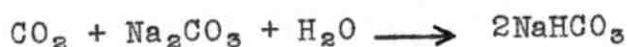
It is quite possible, though, that chromophoric isomers are formed alongside with the formation of colloidal sulfur. Not enough experimental evidence is however available to confirm or invalidate this possibility.

A third possible reason for the blue colour in the KSCN melt would be the formation of free electrons. A brief investigation however has shown that no such free electrons were to be found in the coloured melts of KSCN.

## APPENDIX

### Sodium Carbonate-Phenolphthalein Test <sup>26</sup>

This test depends upon the fact that phenolphthalein is turned pink by soluble carbonates and colourless by soluble bicarbonates. Hence if the carbon dioxide liberated by dilute acids from carbonates is allowed to come into contact with phenolphthalein solution coloured pink by sodium carbonate solution, it may be identified by the decolourisation which takes place:



The concentration of the sodium carbonate solution must be such as not to be decolourised under the conditions of the experiment by the carbon dioxide of the atmosphere.

#### Procedure:

Place 1-2 drops of the test solution (or a small quantity of the test solid) in the test tube shown in Fig. 5

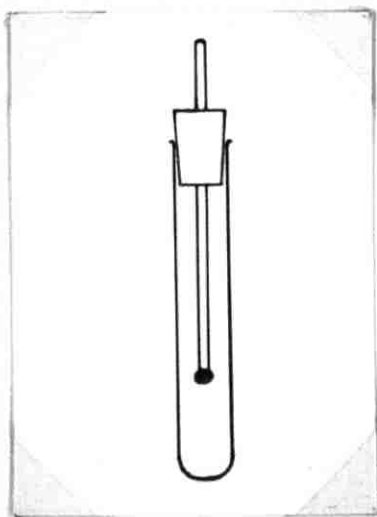


Fig. 5

and place a drop of the sodium carbonate-phenolphthalein reagent on the knob of the glass rod. Add 3-4 drops of 2N H<sub>2</sub>SO<sub>4</sub> and insert the stopper into position. The drop is decolourised either immediately or after a short time according to the quantity of carbon dioxide formed. A blank test is performed in a similar apparatus.

Sensitivity:

4 µg CO<sub>2</sub> (in 2 drops of solution). Concentration limit is 1 in 12,500.

Reagents:

The reagent is prepared by mixing 1 ml of 0.1N sodium carbonate with 2 ml of a 0.5 per cent solution of phenolphthalein and 10 ml of water.

Interfering Substances:

Sulfides, sulfites, thiosulfates, cyanides, cyanates, fluorides, nitrites and acetates interfere. The sulfur containing anions can be quantitatively oxidized to sulfates by hydrogen peroxide:



The modified procedure in the presence of these anions is therefore to stir a drop of the test solution with 2 drops of 30 volume hydrogen peroxide, then to add 2 drops of 2N H<sub>2</sub>SO<sub>4</sub> and to continue as above. Cyanides are rendered innocuous by treating the test solution with 4 drops of a saturated

solution of mercuric chloride, followed by 2 drops of sulfuric acid, etc.; the slightly dissociated mercuric cyanide is formed. Nitrites can be removed by treatment with aniline hydrochloride.

### Sodium Nitroprusside-Zinc Sulfate Test <sup>27</sup>

Sodium nitroprusside solution reacts with a solution of a zinc salt to yield a salmon-coloured precipitate of zinc nitroprusside  $Zn [Fe(CN)_5NO]$ . The latter reacts with moist sulfur dioxide to give a red compound of unknown composition; the test is rendered more sensitive when the reaction product is held over ammonia vapour which decolourises the unused zinc nitroprusside.

#### Procedure:

Place a drop of the test solution in the tube of Fig. 5 and coat the knob of the glass stopper with a thin layer of the zinc nitroprusside paste. Add a drop of 2N HCl or  $H_2SO_4$  and close the apparatus. After the sulfur dioxide has been evolved, hold the stopper for a short time in ammonia vapour. The paste is coloured more or less deep red.

#### Sensitivity:

3.5  $\mu g$   $SO_2$ . Concentration limit is 1 in 14,000.

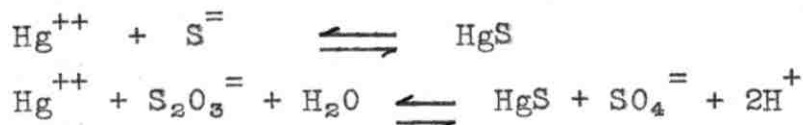
#### Reagents:

The zinc nitroprusside paste is prepared by precipitating sodium nitroprusside solution with an excess of  $ZnSO_4$  solution and boiling for a few minutes; the precipitate is

filtered and washed, and kept in a dark brown bottle.

Interfering Substances:

The test is not applicable in the presence of sulfides and / or thiosulfates. These can be removed by the addition of mercuric chloride, which reacts forming the acid stable mercuric sulfide:



Procedure:

Place a drop of the test solution and 2 drops of saturated mercuric chloride solution in the same apparatus and after a minute, acidify with 2N HCl or H<sub>2</sub>SO<sub>4</sub> and proceed as above.

20 µg of Na<sub>2</sub>SO<sub>3</sub> can be detected in the presence of 900 µg of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and 1,500 µg of Na<sub>2</sub>S.

Nickelous Hydroxide Test<sup>28</sup>

The auto-oxidation of sulfur dioxide (or sulfurous acid) induces the oxidation of green nickelous hydroxide to the black nickelic hydroxide. The colour change is quite distinct, but for very small amounts of sulfur dioxide use may be made of the conversion of benzidine acetate to "benzidine blue" by the higher nickel oxide. Thiosulfates give a similar reaction and must therefore be absent; sulfides also interfere.

Procedure:

Place a drop of the test solution (or a little of the test solid) in the same tube of Fig. 5 and place a little washed nickelous hydroxide on the glass knob under the stopper. Add 1-2 drops of 5-6N HCl, close the apparatus and warm gently. The green hydroxide turns grey to black according to the amount of sulfite present. For small amounts of sulfites, transfer the nickel hydroxide to a quantitative filter paper and treat with a drop of the benzidine reagent; a blue colour is formed.

An alternative technique is to warm (water bath) the test solution in a semimicro test tube with a little dilute hydrochloric acid and expose the evolved gas to filter paper upon which a stain of nickelous hydroxide has been made. The stain acquires a black colour.

Sensitivity:

0.4  $\mu\text{g}$   $\text{SO}_2$ . Concentration limit is 1 in 125,000.

Reagents:

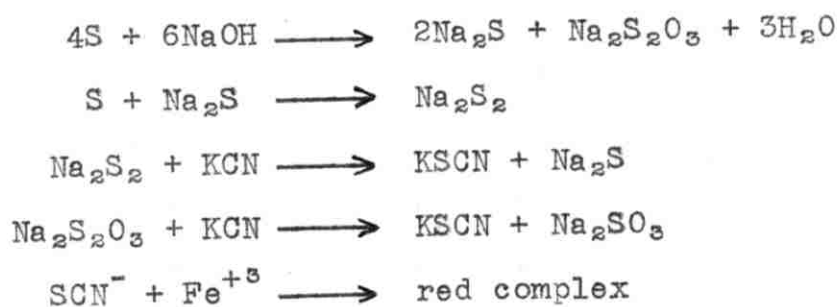
The nickelous hydroxide is prepared by precipitating nickelous chloride solution with sodium hydroxide solution and washing thoroughly until free from alkali. It should be freshly prepared.

The benzidine reagent is prepared by dissolving 0.05 gram of benzidine or of its hydrochloride in 10 ml of glacial acetic acid, diluting to 100 ml with water and filtering.

29

Test for Free Sulfur by Conversion into Thiocyanate

Free sulfur is converted into sulfide, polysulfide, and thiosulfate by boiling with alkali hydroxide. Evaporation of polysulfide and thiosulfate with a solution of KCN produces  $\text{SCN}^-$  which is easily detected by its reaction with  $\text{FeCl}_3$ .



Procedure:

Few milligrams of solid are placed in a crucible with few drops of dilute NaOH and are cautiously evaporated to dryness over a very small flame. The evaporation is repeated after the addition of a few drops of 0.1% KCN solution. The residue is taken up with dilute  $\text{H}_2\text{SO}_4$  and  $\text{Fe}^{+3}$  is added.

30

Thallium Polysulfide Test

Procedure:

Prepare fresh Thallium sulfide paper by bathing filter paper whatmann 42 in 0.5% thallium carbonate or thallium acetate solution for several minutes. The liquid is allowed to drain off and the paper is dried in a blast of hot air.  $\text{Tl}_2\text{S}$  is deposited by placing the paper across a beaker containing  $(\text{NH}_4)_2\text{S}$  warmed at  $80^\circ\text{C}$ . The conversion to sulfide is

rapid; the paper turns black on the side exposed to the fumes. Cut into strips and use immediately.

Spot the strip with a drop of the solution to be tested for free sulfur. The solvent ( $\text{CS}_2$  or pyridine) is allowed to evaporate at room temperature or is removed by a blast of hot air. The spotted paper is then placed in 0.5N  $\text{HNO}_3$  and swirled. If no sulfur is present the whole paper turns white in about 30 seconds. If a brown fleck is left sulfur is present.



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