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**THE DEW POINTS OF ACIDIC  
VAPOURS IN SIMULATED POWER  
STATION FLUE GASES.**

by

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## **ABSTRACT**

During combustion sulphur and chlorine, which are present as the major impurities in fuel oil and coal, are partially converted into sulphuric acid and hydrochloric acid respectively. Condensation of such corrosive products is clearly highly undesirable and regions of plant have been identified where acid dewpoint corrosion impinges upon the efficiency and maintenance cost of oil and coal fired power stations.

It is further recognised that prevention of acid deposition can be achieved if the flue gas temperature is maintained above the acid dewpoint. However, expulsion of flue gas at temperatures higher than the acid dew point decreases the energy yield from the fuel and is therefore wasteful and uneconomic. Clearly, precise determination of the acid dewpoint is vital.

A literature survey showed that dewpoint data for the  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  system have considerable scatter within a range  $\pm 10$  K. Recently, Halstead and Talbot (CERL-Leatherhead) have developed an -

equilibrium gas saturation technique which gives an uncertainty of only  $\pm 2$  K. There remains however some doubt about the estimate of the enthalpy of vaporisation of sulphuric acid. Furthermore little is known about the poten-

tially more interesting three component system  
 $\text{H}_2\text{SO}_4/\text{HCl}/\text{H}_2\text{O}$ .

This work has sought to tackle these deficiencies by applying an improved version of Halstead and Talbot's transpiration apparatus to dewpoint investigations in the  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  system and to the  $\text{H}_2\text{SO}_4/\text{HCl}/\text{H}_2\text{O}$  system.

The results obtained essentially confirm Halstead and Talbot's findings in the  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  system and enabled a more precise determination of the vaporisation enthalpy of sulphuric acid. Very importantly, it has been established that the dewpoint is independent of the presence of HCl.

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## **1.0 GENERAL INTRODUCTION**

### **1.1.1 MAIN SOURCES OF ENERGY TO PRODUCE ELECTRICITY**

The main energy sources used to produce electricity are coal, oil, natural gas, hydro and nuclear energy. Small amounts of energy are produced by wind, solar, sea and geothermal sources <sup>(1-2)</sup>. However industrialisation and development throughout the world means that the demand for energy is growing rapidly.

In recent years the various fractions of the major energy resources and fuels to generate electricity in the UK are approximately 80 % coal, 8 % heavy oil, 10% nuclear and 2% others. It can be seen that coal and oil, which contain impurities sulphur and chlorine, form the major source of fossil fuels used in power stations.

## **1.2.1 IMPURITIES IN COAL AND CRUDE OIL**

Any constituent of coal or crude oil which is detrimental to its utilisation as a fuel can be regarded as an impurity. Normally, impurity means any inorganic constituent of coal or oil and any element other than carbon and hydrogen. There are great differences in the amount of impurities present in various sources of coal and oil.

This study is mainly concerned with sulphur and chlorine impurities in coal and oil.

## **1.2.2 THE IMPURITIES IN COAL**

A large part of the impurities in coal is present as actual minerals, in the form of syngenetic and epigenetic types of depositions. Normally classification of these minerals is as follows <sup>(10)</sup>.

**Sulphide group : Pyrites, marcasite**

**Chloride group :Sylvite, halite**

Coal also contains trace quantities of many other minerals. The metallic elements involved are silicon, aluminium, iron, calcium, magnesium, titanium, sodium and potassium.

Table (1.2.1) shows the range of values of the constituent oxides in the ashes of commercial grades of British coals

Constituent Oxide	Minimum value(%)	Maximum value(%)
$\text{SiO}_2$	4	72
$\text{Al}_2\text{O}_3$	4	38
$\text{Fe}_2\text{O}_3$	2	66
$\text{CaO}$	0.5	25
$\text{MgO}$	0.6	9.5
$\text{TiO}_2$	0.1	2.4
$\text{Na}_2\text{O}$	0.2	7.4
$\text{K}_2\text{O}$	0.2	4.6

Table (1.2.1) Metallic oxides in coal<sup>(10)</sup>

### 1.2.3 THE IMPURITIES IN CRUDE OIL

The impurities in crude oil, being different in nature and character, cannot be directly compared with those in coal. Nevertheless, it must be recognised that much of the study of impurities has been made on distillates, and may thus relate to decomposition products rather than to the compounds present in crude oil.

The ultimate analysis of crude oil shows it to consist mainly of carbon and hydrogen and it is therefore properly regarded as mainly hydrocarbon in character. Nevertheless it may contain a considerable amount of sulphur and small quantities of other elements, namely; oxygen, nitrogen, chlorine and a wide variety of metals<sup>(10)</sup>.

#### **1.2.4      SULPHUR IMPURITIES IN COAL**

Sulphur, present both in mineral matter and in organic combination with the coal substance, is one of the most troublesome impurities in coal. In the mineral matter it occurs as pyrites and marcasite, and to a very minor extent as sulphate, usually that of calcium or iron. The remainder of the sulphur is present in organic combination with the coal and has its most probable origin at least partly in the coal-forming plants. Generally it is believed that organic sulphur increases with increasing pyritic sulphur. As a result of the analysis of 2500 British coal samples<sup>(8)</sup>, a correlation was established between organic sulphur and total sulphur. It has been reported that:

- (i) Organic sulphur is normally fairly evenly distributed from floor to roof in a seam
- (ii) Many seams show a fairly consistent organic sulphur content over wide areas
- (iii) There is a tendency for organic sulphur to increase in highly pyritic coals. A sample in New South Wales shows in Table 1.2.2 the distribution of organic and pyritic sulphur in a seam <sup>(10)</sup> where A, B, C, D and E are different layers in a seam.

**SULPHUR (%)**

	Total	Pyritic	Organic
Roof E	5.26	3.60	1.66
D	1.86	0.60	1.26
C	1.79	0.35	1.44
B	3.27	1.68	1.59
Floor A	2.44	0.99	1.49
Unworked coal below seam 1	12.61	11.14	1.47

Table (1.2.2) Distribution of sulphur in a seam <sup>(10)</sup>

## **1.2.5      SULPHUR IMPURITIES IN PETROLEUM**

A minority of crude oil contains less than 0.5 percent sulphur, the majority contains 0.5 - 3.0 percent and some contains more, with a few having as much as 7 percent. The largest part of the sulphur in a crude oil is present as complex high boiling compounds, especially asphaltic constituents, in which the sulphur is believed to act largely as a bridge between aromatic rings. Elemental sulphur and hydrogen sulphide have also been identified in crude oil<sup>(10)</sup> and much is known about the simpler sulphur compounds which are found in the distillates of crude oil.

## **1.2.6      CHLORINE IMPURITIES IN COAL AND PETROLEUM**

The problem of chlorine in coal has come into prominence since 1939 and has received great attention because of the part it plays in the availability of large boilers. The effects of salt had, however, previously been recognised by chlorine influence on carbonisation of refractories, by its corrosive effect on copper components of boilers, particularly of locomotive fire boxes and economisers and by its influence on clinker formation during combustion.

Attention was drawn to the importance of the nature of chlorine. Although the word 'salt' was originally used in connection with chlorine it was found that not all the chlorine was present as halides since there was not sufficient water soluble Na and K to correspond to the total chlorine content. In some cases the amount of alkali in coal corresponded to less than 15 percent of the chlorine. Calcium and magnesium chlorides were present in insignificant amounts. Part of the chlorine exists as ion linkage and some as organic chloride<sup>(10)</sup>. Chlorine occurs in British coals in amounts varying from a trace to 1.2 percent.

Crude oil often becomes contaminated during production especially when the crude is taken underneath the seabeds and transported through the sea. In some countries oil storage containers are often cleaned by sea water.

### **1.3.1 COMBUSTION AND SULPHUR TRIOXIDE FORMATION**

The impurity sulphur burns in oxygen and produce sulphur dioxide (SO<sub>2</sub>) and a small amount of sulphur trioxide (SO<sub>3</sub>). The formation of sulphur trioxide<sup>(9-15)</sup> is mainly due to



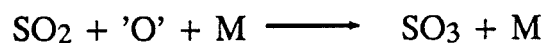
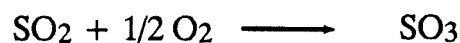
(a) Catalytic oxidation of sulphur dioxide to trioxide on surfaces in the path of the combustion gases.

(b) The formation of the trioxide within the flame itself.

Although much evidence is available to support the first mechanism it could not easily explain the existence of SO<sub>3</sub> within a combustion chamber i.e before the gases come into contact with superheaters and other heat transfer surfaces held responsible for the catalytic action.

The essential difference between the two mechanisms is that the first involves consideration of SO<sub>2</sub> oxidation by reaction with molecular oxygen at a catalyst surface, whereas the second mechanism proposed that SO<sub>2</sub> oxidation takes place by a homogeneous reaction with an oxidising flame species, thought to be oxygen atoms. The formation of SO<sub>3</sub> by heterogeneous catalysis is well known, being used in the manufacture of sulphuric acid.

The mechanism of the reaction of SO<sub>2</sub> with molecular oxygen and atomic oxygen are as follows:



where M is a third body

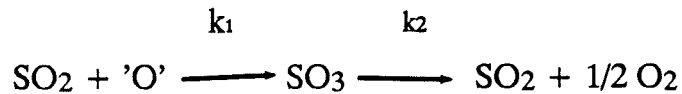
### 1.3.2 THE KINETICS OF SO<sub>3</sub> FORMATION

SO<sub>3</sub> is produced by homogeneous and heterogeneous oxidation of SO<sub>2</sub>. At higher temperatures <sup>(9,14,17)</sup>



The equilibrium 'O' atom concentration is strongly temperature dependent and it can be shown that it increases by 6 orders of magnitude as the temperature increases from 1000' to 2000' K <sup>(14)</sup>

The theory proposed to explain this results was therefore that of a consecutive reaction represented as <sup>(9)</sup>



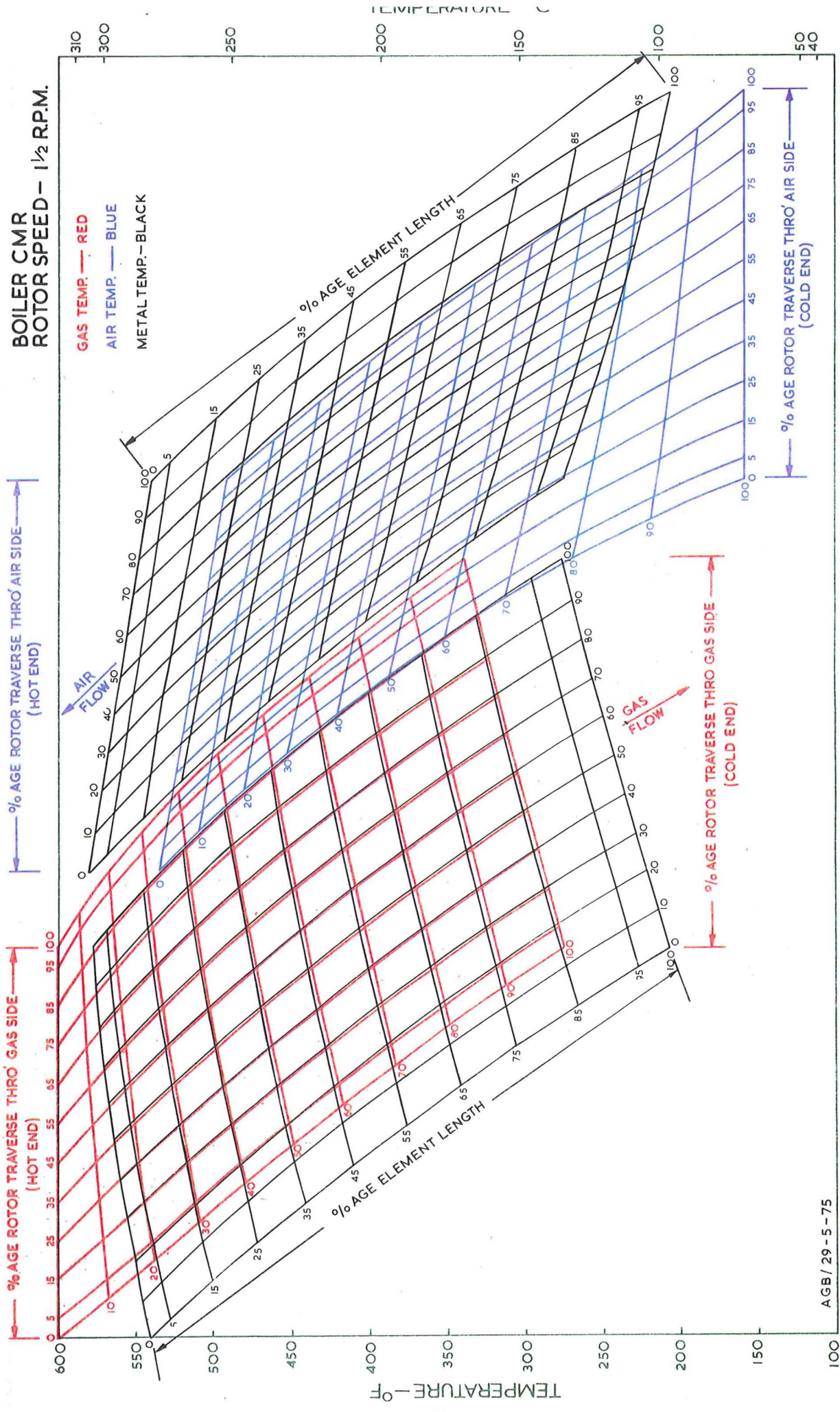
where both reactions were assumed to be first order with the rates dependent solely on [O] and [SO<sub>3</sub>]

concentration respectively with the SO<sub>3</sub> concentration with time being given by the equation <sup>(9)</sup>

$$[SO_3] = \frac{C k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

where k<sub>1</sub> and k<sub>2</sub> are the consecutive reaction rate constants and C is the initial concentration of oxygen atoms in p.p.m.

BOILER CMR  
ROTOR SPEED - 1 1/2 R.P.M.



AGB / 29 - 5 - 75

FAWLEY AIRHEATERS - DESIGN VALUES

Fig (1.3.1) Air heaters temperature range

### **(11) Dissociation of H<sub>2</sub>SO<sub>4</sub> and SO<sub>3</sub>**

The dissociation of H<sub>2</sub>SO<sub>4</sub> vapour into sulphur trioxide depends on the concentration of water vapour in air at atmospheric pressure <sup>(25)</sup>. The sulphuric acid concentration which is appropriate to boiler plant will dissociate completely above 400°C <sup>(25)</sup>. In the meantime sulphur trioxide also starts to dissociate into sulphur dioxide and oxygen above 300°C.

## **1.3.3 ACID FORMATION AND CORROSION**

Almost all the chlorine which is present in fuel is converted into HCl gas during combustion. The sulphur trioxide which is formed during combustion, combines with water molecules and forms sulphuric acid vapour. These vapours start to condense at the back end of the power stations exhaust system, normally within a temperature range of 110°C - 170°C depending on the amount of SO<sub>3</sub> formed during the combustion. The acids start to condense in the air heater section which operates in the above range of temperature as shown in figure (1.3.1).

Deposition of these acids in the plant causes corrosion not only because of the acidic nature of the liquid but also because the liquid acts as a repository for particulate matter

which enhances corrosion. Sometimes, due to excessive fouling of air-heaters, boilers have to be taken out of service so that the air heaters may be cleaned by chemical means. This is expensive and uneconomic.

#### **1.3.4 ECONOMIC SIGNIFICANCE OF SULPHUR AND CHLORINE PROBLEMS**

The problems associated with sulphur and chlorine are faced by all users of coal and oil fired boilers. It has been calculated that the amount of sulphur oxides produced in Britain by transport, industry and energy generation in 1987 were approximately 115,000 tonnes from transport, 1,050,000 tonnes from industry and 2,527, 000 tonnes from energy generation per annum were released into the atmosphere. The sulphur oxides are not only corrosive but are one of the major pollutants and it is now evident that the acid rain problem is a major environmental concern. Forests, lakes and buildings are seriously affected by sulphur pollutants.

The cost of the corrosion damage to zinc coated and painted steel due to emitted sulphur oxides has been estimated on various simplifying assumptions for 12 European countries including the U.K. Tables given there imply 1985 costs of about £2000 M pa for the U.K. only<sup>(7)</sup>.

British gas consumers are estimated to loose about \$200 M Pa in keeping the exit flue gas temperature above the acid condensation temperature in domestic gas boilers. The exhaust system corrosion and failure of internal combustion engines caused by the acid condensate are in the range \$200 - 300 M Pa <sup>(7)</sup>. Furthermore, a substantial amount of energy is wasted in power stations to expel the flue gases above the acid condensation temperature and this is discussed in section 1.5.1

#### 1.4.1 SOLUTIONS TO THE ACID FORMATION PROBLEM

During combustion, SO<sub>2</sub>, SO<sub>3</sub> and HCl are formed in the flue gas. The formation of HCl only depends on the amount of chlorine in the fuel. However the conversion of SO<sub>2</sub> to SO<sub>3</sub> depends on many factors; the nature of the sulphur presence in the fuel, the extent of the air excess used during combustion, flame temperature etc.

The effects of plant corrosion and air pollution from SO<sub>2</sub>, SO<sub>3</sub> and HCl, clearly show the importance of controlling their formation.

This could be achieved by

- (i) The removal of the sulphur and chlorine from the fuel
- (ii) Control of the SO<sub>2</sub> formation in the combustion zone by (a) controlling excess air during combustion (b) neutralising additives
- (iii) The use of flue gas desulphurization systems (FGD)

## **1.4.2      SULPHUR REMOVAL FROM COAL AND PETROLEUM**

Normally pyrites sulphur in coal is not uniformly distributed. However, attempts to separate discrete lumps of pyrites by float/sink methods from the coal as mined have been largely unsuccessful. In this method the coal is first pulverised. It is assumed that pyrites will be present in the form of individual particles, each of which is relatively pure pyrites. Pyrites has a relative density of approximately 5 and coal has a relative density which varies from 1.2 to 1.8 according to rank. This physical difference is used in a mechanical process which separates pyrites from coal.

In some countries a thermo-magnetic separation method has been used where the coal undergoes a brief heat-treatment during which oxidation of the surface of pyrites grains occurs with the formation of thin films of magnetic oxide and sulphate.

In the case of petroleum the first consideration is whether to desulphurize the fuel oil or to desulphurize the entire crude. The latter route offers many extra advantages which seem to be preferable. By desulphurizing before crude distillation, corrosion of refinery equipment is greatly reduced. Hydro desulphurization appears to be one of the most likely prospects for desulphurizing crude at reasonable cost. The process should operate at relatively low pressure, preferably below  $1,000 \text{ lb/in}^2$ , and a catalyst should be used to encourage the reaction.

### **1.4.3 CHLORINE REMOVAL FROM COAL AND PETROLEUM**

The National Coal Board and Central Electricity Generating Board <sup>(10)</sup> have carried out experiments to establish whether water soluble chlorine can be removed by coal washing processes and by exposure to rain. They have found that normal coal washing brought about little reduction, partly because of the contamination of the wet coal



by the chlorides which accumulated in the washing water. Exposure to rain may, under favourable circumstances, bring about a substantial reduction in the chlorine content. The chlorine content of a stock of 1 m m washed smalls fell from 1.1 to 0.3 percent after 3 years storage. The water soluble chlorine in petroleum can also be removed by water washing<sup>(10)</sup>. However the organically combined chlorine is difficult to remove and uneconomic in both coal and petroleum.

#### **1.4.4 EFFECT OF EXCESS COMBUSTION AIR**

In a series of investigations at four power stations, J.W Laxton and R.S Jackson<sup>(10)</sup> obtained an approximately linear relationship between the proportion of excess combustion air and measurements of acid deposition rate. This established the importance of limiting the proportion of excess oxygen in flue gas by appropriate combustion control.

<b>Power Station</b>	<b>Mean excess oxygen %</b>	<b>Acid deposition rate</b>
	(v/v)	(vpm)
<b>South Deans</b>	2.2	2,960
	1.3	1,250
	1.1	360
<b>Plymouth</b>	2.8	1,300
	2.7	1, 200
	1.9	500
	1.2	150

Table (1.4.1) Measurement of acid deposition rate at South Deans and Plymouth B power stations <sup>(10)</sup>

Acid deposition rate for a given oxygen concentration varies greatly between boilers. For example, at 1.5 % excess oxygen the acid deposition rates at Plymouth, South Deans and Marchwood power station were 330, 870, and 1,470 units respectively. This observation is important since it shows that the corrosive nature of flue gas is affected markedly by some operational or design factor other than the proportion of excess combustion air.

## **1.4.5 NEUTRALISING ADDITIVES**

Numerous neutralising additives have been injected at various points in a boiler and its exhaust system to combat sulphur trioxide formation. Although such additives are effective, the overall SO<sub>3</sub> reduction is only 5 percent or less<sup>(10)</sup>. Inefficient methods of mixing additives with the combustion products are probably responsible.

### **(i) Effect of injecting zinc**

More recently metallic additives have been injected into combustion chambers so that the burning metal will react preferentially with atomic oxygen and reduce the tendency for SO<sub>3</sub> to be formed<sup>(10)</sup>. The resultant basic oxides then act as neutralising additives.

### **(ii) Effect of injecting ammonia**

Ammonia has been injected into economisers or air heaters to neutralise sulphuric acid<sup>(11)</sup> but this must be carried out at exactly the right temperature. If the temperature is too high, ammonium bisulphate is formed. This is corrosive and difficult to remove. This method has some practical difficulties due to the nature of concentrated ammonia and which is hazardous to personnel.

### **(iii) Effect of injecting magnesium**

Magnesium compounds were chosen as additives because the oxide and hydroxide can be stored without serious deterioration and because they are available in fine par-

ticulate form (with high surface area). In addition, the low atomic weight of magnesium minimises the amount of material required and the solids burden emitted<sup>(16)</sup>.

Magnesium possesses three immediate advantages over zinc as an additive. It has a much lower atomic weight and magnesium oxide increases the melting point of deposits on high temperature heat exchange surfaces<sup>(10)</sup>.

#### **1.4.6 FLUE GAS DESULPHURIZATION (FGD)**

There are over one hundred different flue gas desulphurization processes available or in various stages of development, ranging from small laboratory-scale to full-scale commercial units. A detailed review of FGD processes has been published by Kyte<sup>(28)</sup>.

In spite of the efforts to develop environmentally attractive processes that make marketable products, the lime/limestone slurry scrubbing process still dominates the commercial market for flue gas desulphurization.

The limestone slurry scrubbing process requires only three pieces of major equipment: an absorber, a hold tank and a liquid/solid separator.

However within this simple framework occur many interacting role processes including gas/liquid mass transfer with chemical reaction, limestone dissolution and crystallisation and sulphate oxidation. Therefore, although it is easy to design and construct a limestone slurry scrubbing process it can be much more difficult to design and operate an optimal system.

There is still active development of alternatives to throwaway slurry scrubbing. Regenerable processes such as MgO scrubbing minimise waste production. However each of these new processes includes many of the same physical and chemical processes as in throwaway slurry scrubbing. In addition, there are new problems in solution equilibria gas/ solid reactions, temperature, side reactions and other phenomena that must be dealt with in each new process.

## **1.5.1**

### **AIMS OF THIS PROJECT**

#### **(i) Problems**

Whatever steps are taken to avoid the sulphur problem, about 5 - 100 vpm  $\text{SO}_3$  is still found in the flue gases.

When flue gases are cooled below a certain temperature a liquid phase starts to appear. This liquid phase has been found to contain about 75% - 85% sulphuric acid. The presence of  $\text{H}_2\text{SO}_4$  vapour increases the temperature at which exhaust gases must leave the plant if separation of a condensed liquid phase in the –

plant is to be prevented. The condensed liquids are not only corrosive but also act as a repository for particulate matters which may enhance corrosion.

#### **(ii) Consequences**

In general it is well known that for the  $\text{SO}_3$  concentration in typical flue gases, condensation occurs in the range  $120^\circ$  -  $170^\circ$  C. If any areas of carbon steel plant ducts, stack linings, air heaters etc were operated below this temperature range, corrosion rates in the range 0.1 - 5.0 mm/yr would occur <sup>(3)</sup>. To avoid this potentially expensive situation power generation plant is invariably operated so that the exit flue gases are not cooled below the acid condensation temperature (acid dew point).

Expulsion of flue gases at higher temperatures than the dew point decreases the energy yield from the flue gases and is therefore wasteful and uneconomic. A 20°C reduction in exit gas temperature from the final heat recovery plant could provide an additional 0.32 percentage in generation efficiency (normally 35 to 35.32%). If this could be obtained over the whole coal burn of 80 m ton p.a. in the U.K, power stations savings of about £30 M p.a. would result<sup>(4)</sup>.

Clearly if the concentration of SO<sub>3</sub> in the gases is known, the power station operator should be able to predict the precise dewpoint temperature.

A literature survey by Evans and Targett<sup>29</sup> showed measured dewpoint temperature scattered as shown in fig(1.5.1). The influence of HCl on the SO<sub>3</sub> dewpoint is not known.

The aims of this projects were :

- (a) To measure the acid dewpoints as precisely as possible
- (b) To develop a prediction method to obtain dewpoints for any concentration of SO<sub>3</sub>
- (c) To study the influence of HCl on the SO<sub>3</sub> dewpoint temperature.

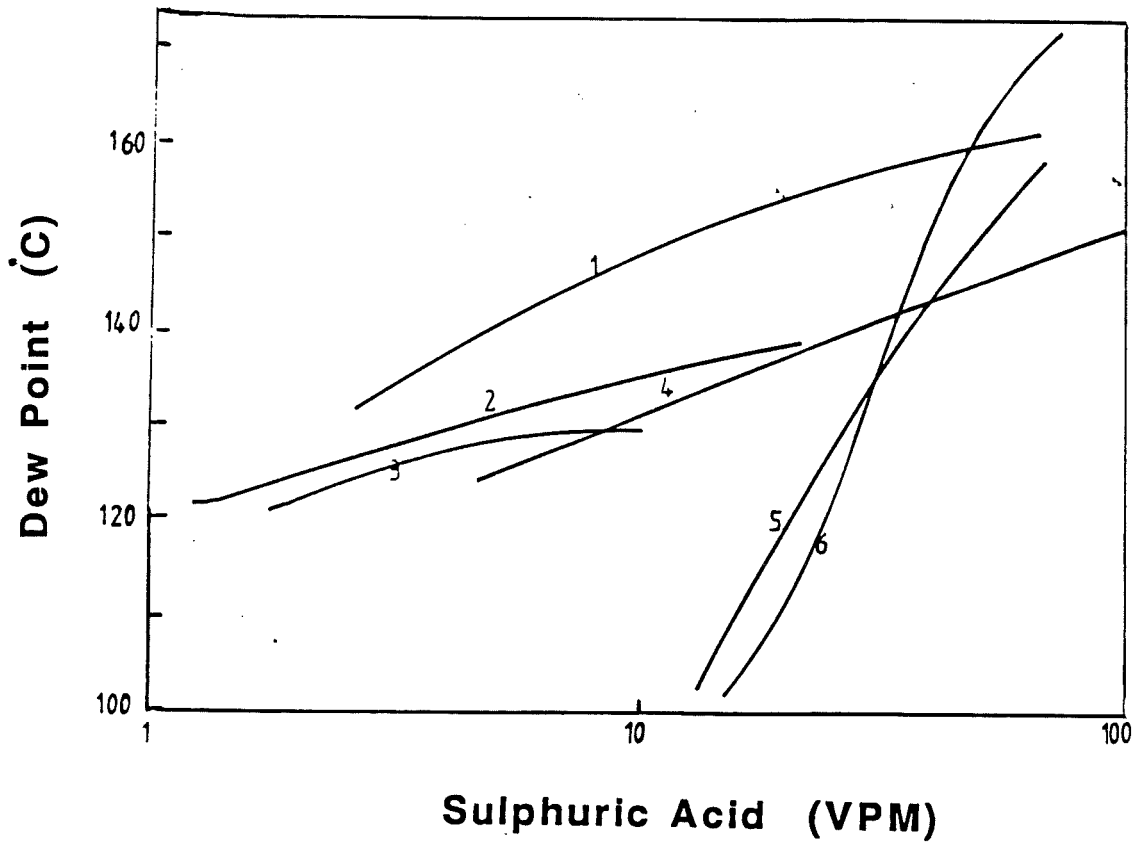


Fig (1.5.1) Experimental dew point curves by different workers.

- (1) Rylands and Jenkinson (51)
- (2) Goksoyr and Ross (52)
- (3) Francis (25)
- (4) Evans and Targett (29)
- (5) Taylor (50)
- (6) Dooley and Whittingham (59)



## **2.1 DEWPOINT**

### **2.1.1 DEFINITION OF DEWPOINT**

The dewpoint is the temperature at which a liquid phase and vapour phase are in equilibrium.

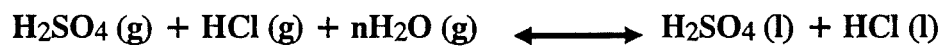
In nature, the effect is most frequently seen when water vapour condenses as the air becomes saturated and is deposited on the leaves of plants. Typical atmospheric water vapour levels are 0.5% to 1% giving dewpoint temperatures of 0° to 10° C

In the case of flue gases in power stations, which normally contain approximately 10% water vapour, dewpoint temperatures of approximately 40° C are expected. The situation is however complicated by the presence of other condensable constituents in addition to water vapour, ie the presence of sulphur trioxide and hydrogen chloride which increase the dewpoint temperature to between 120° C to 170° C

It has been well established that the dewpoint temperature of flue gases depends mainly on the concentration of sulphur trioxide and the equilibrium established in the flue gases is expressed as<sup>(5)</sup>



Nowadays the presence of HCl in flue gases is increasing due to a high chlorine content in the fuel. It is not known whether the presence of HCl affects the above equilibrium or if there is an additional equilibrium present as



### 2.2.1 PHASE RULE AND H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O SYSTEM

The Gibbs phase rule is commonly expressed in the form

$$f = c - p + 2$$

where

f is the number of degrees of freedom,

c is the number of independent components in the system

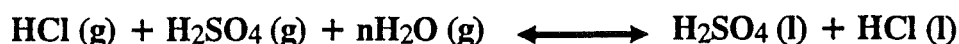
and

$p$  is the number of phases in the system

Sulphuric acid is a mixture of  $H_2O$  and  $H_2SO_4$  and they form a completely mixible azeotropic mixture and have a maximum boiling point. The system has two independent components  $H_2SO_4$  and  $H_2O$  therefore  $c = 2$  and has two phases, one the liquid phase and the other is the vapour phase, therefore  $p = 2$ . From Gibbs phase rule the  $H_2SO_4/H_2O$  system has therefore two degrees of freedom. Since the system under consideration has two degrees of freedom, specification of any two of the parameters; partial pressure of  $H_2O$ , partial pressure of  $H_2SO_4$ , temperature, concentration, will fix the other two.

### 2.3.1 THREE COMPONENT SYSTEM HCl/H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O

If there is an equilibrium present for

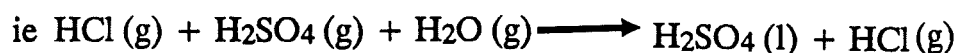


In applying the Gibbs phase rule, we have two phases but the components involved in the equilibrium are not well known.

The component - c is defined in Gibbs phase rule as the number of components of a system at equilibrium ie the smallest number of independently

variable constituents by means of which the composition of each phase present can be expressed either directly or in the form of chemical equation <sup>(22)</sup>.

Therefore if the equilibrium is dependent on HCl then the number of degrees of freedom is three and if the equilibrium is independent of HCl



then the number of degrees of freedom is two

## 2.3.2 SOLUBILITY OF HCl IN SULPHURIC ACID

The solubility of HCl in concentrated sulphuric acid at room temperature is very low as can be seen in the solubility Table (2.3.1) <sup>(26)</sup>

The range we are interested is normally w/w H<sub>2</sub>SO<sub>4</sub> 75 - 90% and we see that HCl has very little solubility at room temperature. At higher temperatures the solubility is not known

H <sub>2</sub> SO <sub>4</sub> % w/w in water	HCl w/w %
0	41.36
5	38.6
10	35.6
15	32.8
20	29.8
25	27.0
30	24.3
35	21.7
40	18.7
45	15.7
50	12.9
55	10.1
60	7.4
65	4.8
70	2.7
76.4	0.36
81.9	0.14
86.8	0.097
89.3	0.092
90.7	0.108

Table (2.3.1) The amount of HCl solubility in sulphuric acid at room temperature <sup>26</sup>.

The relationship between the solubility of HCl in sulphuric acid mixtures is shown by G P Lvchinskii and A I Likhacheva <sup>(26)</sup> in Fig (2.3.1). This curve can be considered as two parts. One a straight line for 0 to 73% H<sub>2</sub>SO<sub>4</sub> and from 73% to 100% a part showing very little solubility. In the same paper, reference is also made to the fact that the solubility of HCl does not obey the Henry - Palton law.

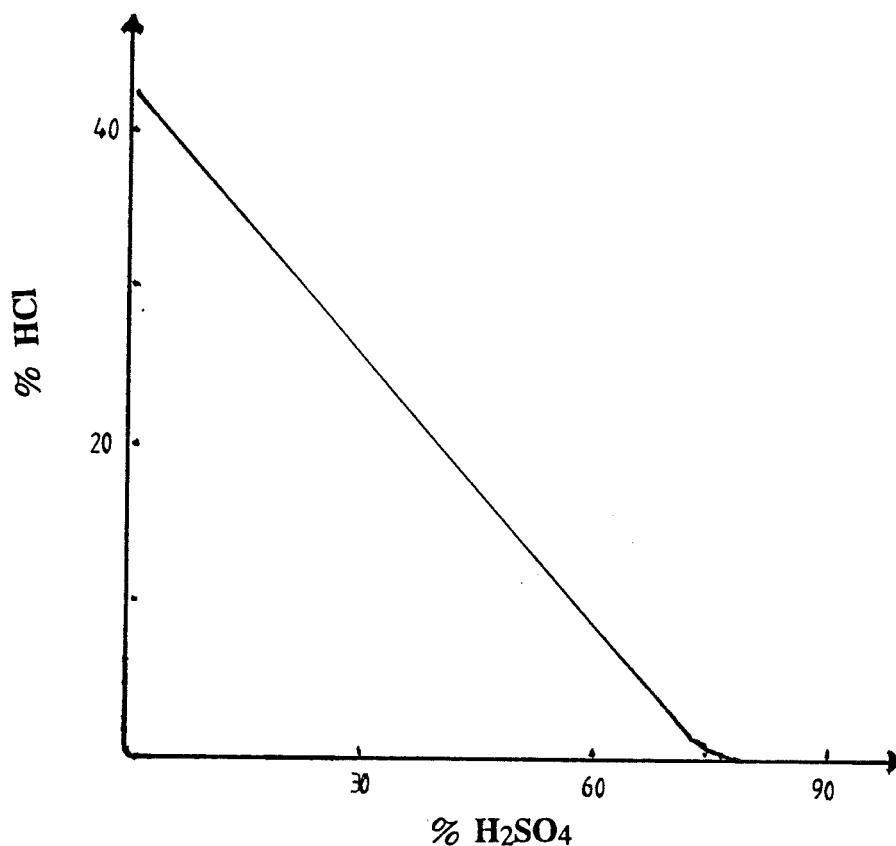


Fig (2.3.1) HCl solubility in sulphuric acid at atmospheric pressure and temperature <sup>26</sup>.

## 2.4.1 VAPOUR PRESSURE IN RELATION TO LIQUID PHASE COMPOSITION

The projection of vapour pressure in a concentration triangle <sup>(26)</sup> Fig (2.4.1) shows that it never reaches the side HCl - H<sub>2</sub>SO<sub>4</sub> and at high concentration of sulphuric acid the isobar are all compressed especially closely to another. It is well known that the solubility of HCl in water is high but on the other hand the solubility of HCl in sulphuric acid is very low. This mainly determines the position of the isobar on the diagram at nine different pressures :

0.08, 0.42, 10.5, 45, 58, 230, 400, 760 mm Hg

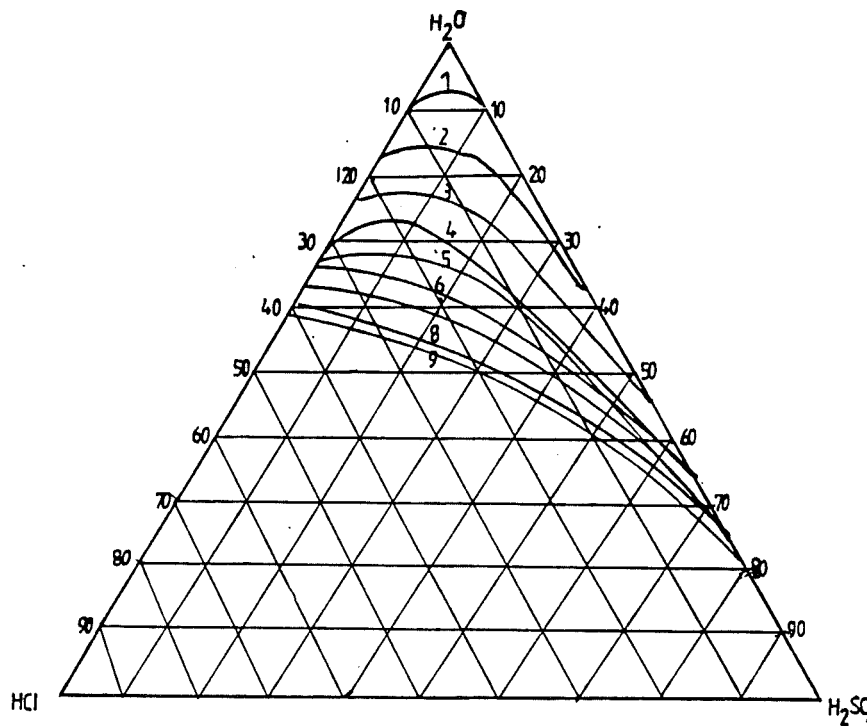


Fig (2.4.1) HCl-H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O solubility triangle at room temperature <sup>26</sup>.

## 2.5.1

# THERMODYNAMICS OF THE EQUILIBRIUM SYSTEM

The thermodynamic relationship controlling the equilibrium vapour pressure of H<sub>2</sub>O or H<sub>2</sub>SO<sub>4</sub> above particular two component H<sub>2</sub>O/H<sub>2</sub>SO<sub>4</sub> system solution at a temperature of T(K) is shown below, with superscript (i) referring to H<sub>2</sub>O or H<sub>2</sub>SO<sub>4</sub>. By definition, T is the dewpoint of a gaseous phase in which H<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub> have partial pressure of p<sub>H<sub>2</sub>O</sub> and p<sub>H<sub>2</sub>SO<sub>4</sub></sub> respectively.

$$R \ln \frac{p_i}{p^*}(T, X) = S_i^\circ - \bar{S}_i(X) + \frac{1}{T} [\bar{L}_i(X) - \Delta H_i^\circ]$$

$$+ \int_{298}^T \frac{1}{T^2} \left[ \int_{298}^T (C_{p_i}^\circ(T) - \bar{C}_{p_i}(T, X)) dT \right] dT \quad 1.$$

where  $i = \text{H}_2\text{O or H}_2\text{SO}_4$

### Superscripts

O = pure component

$\bar{\quad}$  = (overscore) partial molar quantity

298 = property at 298.15K

### Notations

p<sub>i</sub> partial pressure of component i at a temperature T

p\* 101 325 p<sub>a</sub>

S<sub>i</sub><sup>o</sup> the molar entropy of the pure component in the gaseous phase at STP

$\bar{S}_i$  the partial molar entropy in liquid phase at STP

$\bar{L}_i$  the relative partial molar enthalpy of liquid phase (relative to the molar enthalpy of the pure liquid) at STP

ΔH<sub>i</sub><sup>o</sup> the molar enthalpy of vaporisation of the pure component at STP

C<sub>p<sub>i</sub></sub><sup>o</sup> the molar heat capacity of the pure component in gaseous phase at 1 atm and at temperature T



- $\bar{C}_{p_i}^\circ$  the partial molar heat capacity in the liquid phase at 1 atm and temperature T.
- R molar gas constant
- T temperature of the equilibrium in Kelvin
- X mole fraction

## 2.5.2 DERIVATION OF THE THERMODYNAMIC EQUATION

The above equation (1) can be derived from basic thermodynamic relationships. Since this derivation is not easily found in the literature it is given in full below.

The heat capacity of a pure component is normally given by [27]:

$$\left[ \frac{dH_i^\circ}{dT} \right]_p = C_{p_i}^\circ$$

integrating in the range 298 to T

$$\int_{298}^T dH_i^\circ = \int_{298}^T C_{p_i}^\circ dT$$

$${}^T H_i^\circ = {}^{298} H_i^\circ + \int_{298}^T C_{p_i}^\circ dT \quad 2.$$

The Gibbs function is defined by

$$G = H - TS$$

$$\therefore \frac{G_i^\circ}{RT} = \frac{H_i^\circ}{RT} - \frac{S_i^\circ}{R} \quad 3.$$

differentiating w.r.t T

$$\frac{d}{dT} \left[ \frac{G_i^\circ}{RT} \right] = - \frac{H_i^\circ}{RT^2}$$

integrating in the range 298.15 to T

$$\frac{{}^T G_i^\circ}{RT} = \frac{{}^{298} G_i^\circ}{298.R} - \int_{298}^T \frac{{}^T H_i^\circ}{RT^2} dT \quad 4.$$

Combining 2 and 4 gives

$$\frac{{}^T G_i^\circ}{RT} = \frac{{}^{298} G_i^\circ}{298.R} - \int_{298}^T \frac{{}^{298} H_i^\circ}{RT^2} - \int_{298}^T \frac{1}{RT^2} \left\{ \int_{298}^T {}^T C_{P_i}^\circ \cdot dT \right\} dT$$

$$\frac{{}^T G_i^\circ}{RT} = \frac{{}^{298} G_i^\circ}{298.R} + \left[ \frac{{}^{298} H_i^\circ}{RT^2} \right]_{298}^T - \int_{298}^T \frac{1}{RT^2} \left\{ \int_{298}^T {}^T C_{P_i}^\circ \cdot dT \right\} dT$$

$$\frac{{}^T G_i^\circ}{RT} = \frac{{}^{298} G_i^\circ - {}^{298} H_i^\circ}{R \cdot 298} + \frac{{}^{298} H_i^\circ}{RT} - \int_{298}^T \frac{1}{RT^2} \left\{ \int_{298}^T {}^T C_{P_i}^\circ \cdot dT \right\} dT \quad 5.$$

Combining 3 and 5 gives

$$\frac{{}^T G_i^\circ}{RT} = - \frac{{}^{298} S_i^\circ}{R} + \frac{{}^{298} H_i^\circ}{RT} - \int_{298}^T \frac{1}{RT^2} \left\{ \int_{298}^T {}^T C_{P_i}^\circ \cdot dT \right\} dT \quad 6.$$

Applying equation (6) for the vapour phase

$$\frac{{}^T G_i^\circ(v)}{RT} = - \frac{{}^{298} S_i^\circ(v)}{R} + \frac{{}^{298} H_i^\circ(v)}{RT} - \int_{298}^T \frac{1}{RT^2} \left\{ \int_{298}^T C_{P_i}^\circ(v) \cdot dT \right\} dT \quad 7.$$

Similarly applying in the liquid phase for partial molar quantities

$$\frac{{}^T \bar{G}_i^\circ(\ell)}{RT} = - \frac{{}^{298} \bar{S}_i^\circ(\ell)}{R} + \frac{{}^{298} \bar{H}_i^\circ(\ell)}{RT} - \int_{298}^T \frac{1}{RT^2} \left\{ \int_{298}^T {}^T \bar{C}_{P_i}^\circ(\ell) \cdot dT \right\} dT \quad 8.$$

Now for the equilibrium condition, the chemical potentials  $\mu_i$  for the  $i$ th component in each phase must be equal

$$\begin{aligned} \text{i.e.} \quad {}^T\mu_i(\ell) &= {}^T\mu_i(v) \\ {}^T\mu_i(\ell) &= {}^T\mu_i(v) + RT \ln \frac{P_i}{P^*} \\ {}^T\mu_i(v) &= {}^TG_i^\circ(v) \text{ [Gibbs free energy per mole]} \\ {}^T\mu_i(\ell) &= {}^T\bar{G}_i(\ell) \text{ [partial molar Gibbs free energy per mole]} \end{aligned}$$

$$\text{i.e.} \quad {}^T\bar{G}_i(\ell) = {}^TG_i^\circ(v) + RT \ln \frac{P_i}{P^*} \quad 9.$$

Combining 8 and 7 gives

$$\begin{aligned} \frac{{}^T\bar{G}_i(\ell) - {}^TG_i^\circ(v)}{RT} &= \frac{-\left[{}^{298}\bar{S}_i(\ell) - {}^{298}S_i^\circ(v)\right]}{R} + \frac{{}^{298}\bar{H}_i(\ell) - {}^{298}H_i^\circ(v)}{RT} \\ &+ \int_{298}^T \frac{1}{RT^2} \left\{ \int_{298}^T \left[{}^TC_{P_i}^\circ(v) - {}^T\bar{C}_{P_i}(\ell)\right] \cdot dT \right\} dT \end{aligned} \quad 10.$$

Since

$${}^{298}\bar{L}_i(\ell) = {}^{298}\bar{H}_i(\ell) - {}^{298}H_i^\circ(\ell)$$

Combining 9 and 10 gives

$$\begin{aligned} \ln \frac{P_i}{P^*} &= \frac{-\left[{}^{298}\bar{S}_i(\ell) - {}^{298}S_i^\circ(v)\right]}{R} + \frac{{}^{298}\bar{L}_i(\ell)}{RT} - \frac{{}^{298}\Delta H_i^\circ(v/\ell)}{RT} \\ &+ \int_{298}^T \frac{1}{RT^2} \left\{ \int_{298}^T \left[{}^TC_{P_i}^\circ(v) - {}^T\bar{C}_{P_i}(\ell)\right] \cdot dT \right\} dT \end{aligned} \quad 11.$$

where  ${}^{298}\Delta H_i^\circ(v/l) = {}^{298}H_i^\circ(v) - {}^{298}H_i^\circ(l)$

The thermodynamic equation can be reduced to a simple form for the purpose of easy computation as a function of temperature

$$\ln \frac{p}{p^*} = A \ln T + \frac{B}{T} + C + DT + ET^2$$

where

$$A = 1/R [a - \bar{C}_{p298} + 298 \alpha]$$

$$B = 1/R \left[ -\Delta H_{298}^\circ + \Delta \bar{H}_{298} + 298a + b/2(298)^2 + c/3(298)^3 - 298\bar{C}_{p298} + \alpha/2(298)^2 \right]$$

$$C = 1/R \left[ S_{298}^\circ(g) - \bar{S}_{298} - a - b \cdot 298 - c/2(298)^2 + \bar{C}_p 298 \right] - A \ln 298$$

$$D = \frac{1}{2R} [b - \alpha]$$

$$E = c/6R$$

## Reducing the partial pressure equation

$$\ln \frac{p_i}{p^*} = 1/R \left\{ \Delta S_{298}^\circ + (S^\circ(l) - \bar{S}_{298}) - \frac{(\Delta H_{298}^\circ - \Delta \bar{H}_{298})}{T} + \int_{298}^T \frac{1}{T^2} \left[ \int_{298}^T \Delta C_p^\circ dT \right] \cdot dT - \right.$$

$$\left. \int_{298}^T \frac{1}{T^2} \left[ \int_{298}^T \Delta C_p^\circ dT \right] \cdot dT \right\}$$

to

$$\ln \frac{p_i}{p^*} = A \ln T + B/T + C + DT + ET^2$$

Let

$$\ln \frac{P_i}{P^*} = \frac{1}{R} [L + M - N]$$

$$L = \Delta S_{298}^{\circ} + (S^{\circ}(\ell) - \bar{S}_{298}) - \frac{(\Delta H_{298}^{\circ} - \Delta \bar{H}_{298})}{T}$$

$$M = \int_{298}^T \frac{1}{T^2} \left[ \int_{298}^T \Delta C_p^{\circ} dT \right] .dT$$

But  $\Delta C_p^{\circ} = C_p^{\circ}(g) - C_p^{\circ}(\ell)$  and if  $C_p^{\circ}(g) = a + bT + cT^2$

$$\begin{aligned} M &= \int_{298}^T \frac{1}{T^2} \left[ \int_{298}^T [(a + bT + cT^2) - C_p^{\circ}(\ell)] .dT \right] .dT \\ &= \int_{298}^T \frac{1}{T^2} \left[ \left[ (aT + \frac{bT^2}{2} + \frac{cT^3}{3}) \right]_{298}^T - \int_{298}^T C_p^{\circ}(\ell) dT \right] .dT \\ &= \int_{298}^T \frac{1}{T^2} \left[ \left[ (aT + \frac{bT^2}{2} + \frac{cT^3}{3} - a \cdot 298 - \frac{b}{2}(298)^2 - \frac{c}{3}(298)^3) \right] .dT \right. \\ &\quad \left. - \int_{298}^T C_p^{\circ}(\ell) dT \right] .dT \\ &= \left[ a \ln T + \frac{b}{2} T + \frac{c}{6} T^2 + \left[ a \cdot (298) + \frac{b}{2} (298)^2 + \frac{c}{3} (298)^3 \right] \frac{1}{T} \right]_{298}^T - \end{aligned}$$

$$\int_{298}^T \frac{1}{T^2} \left[ \int_{298}^T C_p^{\circ}(\ell) dT \right] .dT$$

$$= = \left[ a \ln T + \frac{b}{2} T + \frac{c}{6} T^2 + \left[ a.(298) + \frac{b}{2} (298)^2 + \frac{c}{3} (298)^3 \right] \frac{1}{T} - a - a \ln 298 - \right.$$

$$\left. b.298 - \frac{c}{2}.298^2 \right] - \int_{298}^T \frac{1}{T^2} \left[ \int_{298}^T C_p^\circ(\ell) dT \right]. dT$$

$$N = \int_{298}^T \frac{1}{T^2} \left[ \int_{298}^T \Delta \bar{C}_p dT \right]. dT$$

But  $\Delta \bar{C}_p = C_p^\circ(\ell) - C_p^\circ(g)$  and if  $\bar{C}_p(\ell) = \bar{C}_{p_{298}} + \alpha (T-298)$

$$N = \int_{298}^T \frac{1}{T^2} \left[ \int_{298}^T \left[ \bar{C}_{p_{298}} + \alpha (T-298) - C_p^\circ(\ell) \right]. dT \right]. dT$$

$$= \int_{298}^T \frac{1}{T^2} \left[ \bar{C}_{p_{298}} \cdot T + \frac{\alpha}{2} T^2 - 298 \alpha T \right]_{298}^T dT - \int_{298}^T \frac{1}{T^2} \left[ \int_{298}^T C_p^\circ(\ell). dT \right] dT$$

$$= \int_{298}^T \frac{1}{T^2} \left[ \bar{C}_{p_{298}} \cdot T + \frac{\alpha}{2} T^2 - 298 \alpha T - \bar{C}_{p_{298}} \cdot 298 + \frac{\alpha}{2} \cdot 298^2 \right]. dT -$$

$$\int_{298}^T \frac{1}{T^2} \left[ \int_{298}^T C_p^\circ(\ell). dT \right]. dT$$

$$= \left[ \bar{C}_{p_{298}} \cdot \ln T + \frac{\alpha}{2} T - 298 \alpha \ln T + \left( \bar{C}_{p_{298}} \cdot 298 + \frac{\alpha}{2} 298^2 \right) \cdot \frac{1}{T} \right] \\ - \int_{298}^T \frac{1}{T^2} \left[ \int_{298}^T C_p^\circ(\ell). dT \right]. dT$$

$$\bar{C}_{P_{298}} \ln T + \frac{\alpha}{2} T - 298 \alpha \ln T + (\bar{C}_{P_{298}} \cdot 298 + \frac{\alpha}{2} 298^2) \cdot \frac{1}{T} - \bar{C}_{P_{298}} \ln 298 + 298 \alpha \ln 298$$

$$- \bar{C}_{P_{298}} - \int_{298}^T \frac{1}{T^2} \left[ \int_{298}^T C_p^\circ(\ell) \cdot dT \right] \cdot dT$$

i.e.

$$A = 1/R [a - \bar{C}_{P_{298}} + 298 \alpha]$$

$$B = 1/R [-\Delta H_{298}^\circ + \Delta \bar{H}_{298} + 298a + b/2 (298)^2 + c/3 (298)^3 - 298 \bar{C}_{P_{298}} + \alpha/2 (298)^2]$$

$$C = 1/R [\Delta S_{298}^\circ + (S_{298}^\circ(\ell) - \bar{S}_{298}) - a - a \ln 298 - b \cdot 298 - c/2 (298)^2$$

$$+ \bar{C}_{P_{298}} \ln 298 - 298 \alpha \ln 298 + \bar{C}_{P_{298}}]$$

$$= 1/R [S_{298}^\circ(g) - S_{298}^\circ(\ell) + S_{298}^\circ(\ell) - \bar{S}_{298} - a - b \cdot 298 - c/2 (298)^2 + \bar{C}_{P_{298}}$$

$$- [a - \bar{C}_{P_{298}} + 298 \alpha] \ln 298]$$

$$= 1/R [S_{298}^\circ(g) - \bar{S}_{298} - a - b \cdot 298 - c/2 (298)^2 + \bar{C}_{P_{298}}] - A \ln 298$$

$$D = 1/R [b/2 - \alpha/2] = \frac{1}{2R} (b - \alpha)$$

$$E = \frac{c}{6R}$$

## **3.0 LITERATURE SURVEY FOR DEWPOINT MEASUREMENT**

### **3.1.1 INTRODUCTION**

The acid dewpoint and the associated low temperature corrosion problem were first identified in the early 20th century. An early acid dewpoint measurement was carried out by Johnstone in 1929 <sup>(42)</sup> using a dewpoint meter. Since then several workers have tried to measure the acid dewpoint precisely by different methods. The methods used can be broadly divided in to four groups

- (1) Dewpoint meter
- (2) Equilibrium compositions
- (3) Thermodynamic calculations
- (4) Microgravimetric

However in a review by Evans and Targett, the acid dewpoint measurements obtained by various workers were found to be scattered as shown in fig (1.5.1) <sup>(29)</sup> This survey looks at the methods used and their advantages and disadvantages.



### **3.2.1 DEW POINT METER**

The version of the dewpoint meter built by Johnstone<sup>(42)</sup> was adopted by the British Coal Utilisation Research Association (BCURA). BCURA developed several versions of the instrument and the device was alternatively called the electrical dewpoint meter, the acid dewpoint meter and the BCURA dewpoint meter.

The dewpoint meter has a detecting element which incorporates a combined thermocouple and electrode assembly mounted on a glass probe. The probe is so designed that the detector can be cooled by means of compressed air. When the detector is introduced into the flue gas, it is cooled gradually until, at the dewpoint, a film of sulphuric acid starts to condense on the detector.

The existence of the film is apparent from the constant electrical conductivity shown by the detector<sup>(50)</sup>. The temperature of the detector in this condition is then measured by means of a thermocouple. This temperature is taken as the dewpoint temperature.

Dewpoint measurements using a dewpoint meter were carried by Taylor(1942)<sup>(50)</sup>, Flint (1948)<sup>(49)</sup>, Fracis(1952)<sup>(25)</sup>, Littlejohn(1952)<sup>(7)</sup>, Kiyoura(1972)<sup>(31)</sup>, and Pcock(1976)<sup>(40)</sup> amongst others. Each worker tried to modify the equipment by improved instrument design and the elimination of instrument errors. The most advanced version of the dewpoint meter is described in British Standard BS 1756.

### **3.2.2 EQUILIBRIUM COMPOSITIONS**

(1)One of the early equilibrium methods was used by Ryland and Jenkinson(1954)<sup>(51)</sup> to determine the acid dewpoint. A mixture of vapour phase and liquid phase was established by evaporating sulphuric acid and mixing with hot air and water vapour. The mixture was then carried through a temperature controlled area, where the liquid phase comes to equilibrium with the gas phase. The liquid phase is collected throughout the experiment and then analysed. This method was later modified by a few others, improving the saturation and using better instrumentation. Using similar methods, experiments were carried out by Haase & Rehse(1959)<sup>(56)</sup> and Haase & Borg mann (1961)<sup>(55)</sup>, covering 44 to 98% concentrated sulphuric acid and 57° to 197°C temperature. Sulphuric acid mixture was vaporised and passed through an equilibrium chamber.

The equilibrium vapour was then displaced through a condenser where it was totally condensed. The condensed liquid was allowed to pass through a conductance cell to determine the composition of the vapour. The equilibrium temperature was then taken as the dewpoint temperature.

## (2) Sampling probe

A different approach was carried out by Goksoyr and Ross (1962)<sup>(52)</sup>, Dooley and Whittingham (1964)<sup>(59)</sup>, Lisle and Sensenbaugh (1965)<sup>(53)</sup>. A known amount of fuel with a constant sulphur content was burned in air. The sulphur trioxide was sampled from the flue gas by using a sampler and condenser. The sample collected was then chemically analysed.

This is then compared with the calibration reading which is based on a gas containing a known quantity of sulphuric acid which is passed through the apparatus at a selected temperature. The amount of acid which is not condensed and passes through the condenser is a measure of the partial pressure of sulphuric acid at the condenser temperature and represents the concentration corresponding to a dewpoint of that temperature.

### **3.2.3 THERMODYNAMIC CALCULATIONS**

An important method of obtaining the acid dewpoint is by thermodynamic calculation. Abel (1945)<sup>(54)</sup> calculated the vapour pressure of sulphuric acid above the liquid system of sulphuric acid and water by using the molar free energy of formation of the gas component which is equal to the partial molar free energy of formation of the liquid component of sulphuric acid.

Thermodynamic calculations were also made by Muller (1959)<sup>(57)</sup> using the chemical potential of each component which are equal in the liquid and vapour phase at equilibrium and combining this – with the Gibbs - Helmholtz equation. These calculation were repeated by Gmitro & Vermeulen (1964)<sup>(42)</sup> and Verhoff & Banchemo (1972)<sup>(58)</sup>.

### 3.2.4 MICROGRAVIMETRIC METHOD

Evans and Targett<sup>(29)</sup> first developed this method in 1976. A known concentration of sulphuric acid was pumped by a peristaltic pump at a rate calculated to give the desired concentration of both sulphuric acid and water vapour. This acid was then vaporised in the range of 300° to 400°C and mixed with nitrogen gas. The mixture was then passed through an ultra microbalance with a sensitivity of 1µm. The mixture was cooled slowly and the temperature was noted at which the weight recorded by the balance started to increase rapidly. This weight increase was allowed to continue for about 15 minutes during which the temperature fell by about another 3°C. Heating was then increased slightly and the condensed acid started to evaporate and the weight started to decrease. By altering the temperature repeatedly the acid dewpoint was measured by a chromel-alumel thermo couple to ± 1°C.

### **3.3.1 ADVANTAGES & DISADVANTAGES OF DEWPOINT MEASUREMENT METHODS**

#### **(1) Dew point meter**

The dew point meter is an attractive method because of its portability and simplicity but there still remain an uncertainty in its reading of the acid dewpoint. The introduction of the dewpoint meter surface at a lower temperature than the dewpoint is vital for acid condensation. A reasonable heat transfer is necessary to cool the gas phase and to withdraw the latent heat of vaporisation.

The accuracy of this method can be maintained only if the temperature is measured when a small amount of liquid acid start to appear in the gaseous phase and the thermal equilibrium is established.

However dewpoint meter cannot detect the onset of liquid acid appearing in the gaseous phase and it requires a substantial amount of acid to form a film which can give a measurable electrical conductivity in the dewpoint meter. Ryland and Jenkinson<sup>(51)</sup> have established this error.

After carrying out hundreds of experiment they came to the conclusion that the acid does not condense initially as a film on the dewpoint meter surface but condenses as tiny droplets when the acid start to form.

According to many early dewpoint meter workers, a gas containing 0.0001% sulphuric acid has a dew point temperature of nearly 120° F, but surprisingly Rylands and Jenkinson, using an equilibrium method, reported that a gas with an identical percentage of sulphuric acid has a dew point temperature of 250° F. This discrepancy clearly indicates that the early workers have overcooled the flue gas to obtain a condensed film.

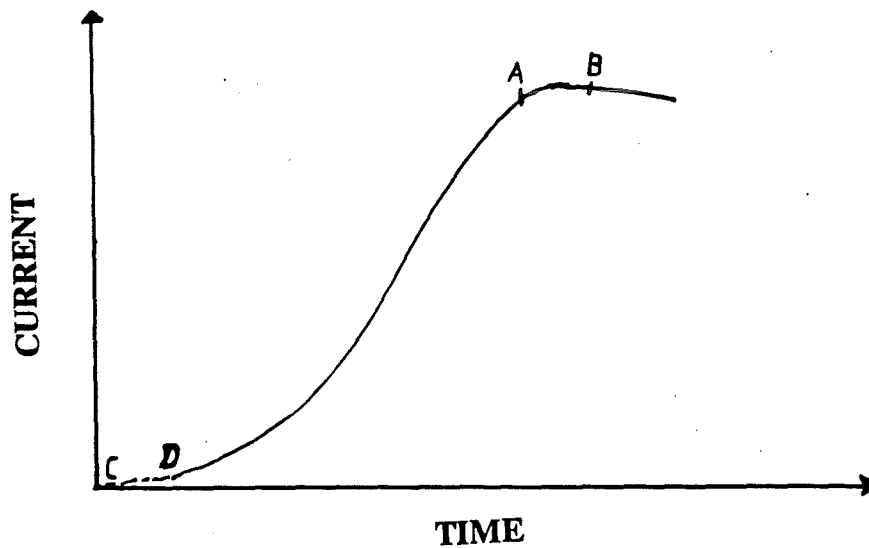


Fig (3.3.1) A typical plot of conductivity change in a dew-point meter.

A typical plot of the conductivity change of the acid film on a dewpoint meter is shown in fig(3.3.1). This shows how the current varies with time as the probe is cooled below the dew point. At C the film between the electrodes is being established and conduction starts. As the probe is progressively cooled the acid film builds up and when established the current reaches a maximum value. Further cooling and fall in temperature of the film causes

a fall in its electrical conductivity. The dewpoint temperature is taken by many workers as the temperature when the conductivity reaches a steady value and starts to decrease ie between A and B.

The technique adopted was to find two temperatures close together at which the conductivity slowly increased and decreased respectively. The dew point was then assumed to lie between these two temperatures. This temperature is obviously lower than the true equilibrium temperature.

After disagreement with calculated data and equilibrium data, some dewpoint meter workers measured

the acid dewpoint by using an extrapolation method as shown in Fig(3.3.1). The curve was extrapolated from D to C and the zero condensation point was estimated. This temperature was taken as dewpoint temperature. This method will depend on the cooling rate.

However British Standard, BS 1756, accepts that the dewpoint meter is unsuitable for low concentrations and the accuracy is stated to be about  $\pm 7^{\circ}\text{C}$ . The above problems make dewpoint meters unreliable even though they are easy to handle.



### **(2a) Equilibrium composition**

Equilibrium composition requires a well established and thermally controlled equilibrium between the vapour and liquid phase. This also requires very effective vapour collection and accurate measurement of air or inert gas pumped

into the system and a good technique for the analysis of the components of the vapour phase. Most of the equipment is glassware which because of its fragile nature is difficult to handle. Also the dewpoint is measured indirectly.

### **(2b) Sampling probe**

This method involves extraction and transportation of the flue gases. The basic difficulty is common to all such flue gas extractive and sampling techniques. The separation of acid from the gaseous phase was attempted by placing some type of filter in the sample entrance of the probe. The problem with a probe filter not only involves the efficiency with which the separation can be achieved, but may well involve the oxidation of sulphur dioxide either on the filter material itself or on the particulates which accumulate on the filter surface during sampling<sup>(41)</sup>.

### **(3) Thermodynamic calculations**

Dewpoint prediction using thermodynamic equations are a very useful way of approaching the problem. They require the values of standard molar entropy, heat capacity, and vaporisation enthalpy for sulphuric acid in the gas

phase and the relative partial molar enthalpy, entropy and heat capacity of sulphuric acid in the liquid phase at the required temperature. Published thermodynamic data for the liquid phase from a number of independent researchers show that the values of the above quantities are in reasonable agreement. However, standard molar values of the gas phase are not so precise. Gmitro and Vermeulen<sup>(42)</sup> used a value of  $300.955 \text{ J mol}^{-1} \text{ K}^{-1}$  for the standard molar entropy of sulphuric acid. JANAF tables (1971)<sup>(46)</sup> give a value of 289.236 where this data is derived from spectroscopic studies on sulphuric acid by Chackalackal and Stafford<sup>(43)</sup> (1965) and Giguere and Savoie<sup>(44)</sup> (1962). This result was also confirmed by Gopinath and Rao. Similarly, heat capacity data can be obtained by rotational and vibrational spectroscopic measurements.

JANAF Tables (1985) published values for  
 $H_f [\text{H}_2\text{SO}_4 (\text{g})] = -735.13 \pm 8.4 \text{ kJ mol}^{-1}$   
and  $H_f [\text{H}_2\text{SO}_4 (\text{l})] = -813.99 \pm 0.67 \text{ kJ mol}^{-1}$

These yield a value for  $\Delta H_{298} [\text{H}_2\text{SO}_4]$  as  $78.86 \pm 9.07 \text{ kJ mol}^{-1}$

This uncertainty in values was a major reason for uncertainty in the calculation of dewpoints. The discrepancies correspond to an uncertainty

approaching  $\sim \pm 25$  K at a dewpoint of  $420^\circ$  K, as noted by Verhoff and Banchero<sup>(58)</sup>.

$\Delta H_{298} [\text{H}_2\text{SO}_4]$  was estimated as  $78.9 \pm 0.01$  kJ mol<sup>-1</sup> by Halstead and Talbot (1975)<sup>(5)</sup> using their 8 sets of experimental data and 91 results from Haase and Borgmann. However doubts remain when using Haase and Borgmann's data. This is analysed in Chapter 5 under 'Result and Analysis'.

#### (4) Microgravimetric method

The microgravimetric determination of dewpoint could be one of the best methods available. However it depends mainly on two factors, namely :

- (a) establishing an equilibrium; and
- (b) monitoring a very small amount of dew when it starts to appear.

Compared to the dewpoint meter, the microgravimetric method is more precise and will detect even a very small amount of acid when dew starts to appear in gaseous phase.

However the method of Evans and Targett<sup>(29)</sup> is not free from defects. For establishing an equilibrium, sulphuric acid was vaporised at  $300^\circ$  to  $400^\circ$  C.

While doing so the authors did not take into

account that, at that temperature sulphuric acid would dissociate into  $\text{SO}_2$  (see section 1.3.2). The loss of 8% sulphuric acid reported by them could be due to the dissociation of sulphuric acid as stated above.

Again the sulphuric acid was pumped in at a constant rate using a peristaltic pump which gives cyclic flow and the characteristics of the pump have also not been reported. The acid was then vaporised and mixed with nitrogen in the vapour phase, but the workers reported difficulties in mixing the vapour and nitrogen in regard to obtaining a uniform mixture. Also the use of a chromel - alumel thermocouple is not satisfactory to measure temperature accurately below  $200^\circ\text{C}$ .

The above method also has the disadvantage of not providing the composition of the acid condensed on the ultra microbalance.

### **3.4.1 HALSTEAD AND TALBOT'S METHOD**

Halstead and Talbot (1975)<sup>(5)</sup> overcame the above problems by using an equilibrium method to estimate  $\Delta H_{298} [\text{H}_2\text{SO}_4]$  and used this value in thermodynamic calculations to estimate the acid dew point for a wide range of conditions. First, they developed a transpiration saturation apparatus as shown in Fig (3.4.1). This apparatus was kept in a thermostatically controlled oil bath.

Argon gas was bubbled through a 5 metre coil into a transpirator and the liquid phase and the vapour phase brought to a dynamic equilibrium. The vapour passed through a delivery tube and was collected efficiently by condensation in collection bottles. By this means Halstead and Talbot measured "a few values of dewpoints". Using these values and Haase and Borgmanns data an estimation of  $\Delta H_{298} (\text{H}_2\text{SO}_4)$  was calculated. Finally this value was used in thermodynamic equations for calculating the dewpoint over a wide range of concentrations.

### **3.4.2 EFFECT OF HCl ON DEWPOINT**

Although of possible importance, the effect of HCl on the acid dewpoint has not been well investigated. This may be due to the uncertainty in measuring the dewpoint of H<sub>2</sub>SO<sub>4</sub> alone which caused investigators not to add an additional component for dewpoint measurement.

However Rylands and Jenkinson (1954)<sup>(51)</sup> carried out a few experiments and reported "The condensation of sulphuric acid and the acid dewpoint were not appreciably affected by the presence of HCl. Kears<sup>(47)</sup> (1955) reported that the presence of HCl affect the dewpoint and dewpoint corrosion below 150°C. Haase and Rehse (1959)<sup>(56)</sup> carried out only two experiments and their result showed a significant variance in the dewpoint of sulphuric acid in the presence of HCl. They also suggested much more work has to be done to confirm their findings.

However in recent research Meadowcroft and Cox<sup>(7)</sup> at CERL, Leatherhead, studied the dewpoint corrosion effect of HCl. Pieces of mild steel were exposed to a flue gas atmosphere containing 15 ppm SO<sub>3</sub>, 1000 ppm SO<sub>2</sub>, 1.3 % excess oxygen with and without 800 ppm HCl added to the flue gas stream. The results showed that the presence of HCl in the flue gas stream had no effect on metal corrosion rates at temperatures above 60°C.

## **4.0 EXPERIMENTAL APPARATUS AND METHOD**

### **4.1.0 INTRODUCTION**

It was decided to adopt an improved version of Halstead and Talbot's method <sup>(5-6)</sup> based on their apparatus. This was provided on loan from Central Electricity Research Laboratory (CERL), Leatherhead.

The method allowed the following

- \* Equilibration of the liquid and vapour phases
- \* Maintenance of a constant equilibrium temperature throughout the experiment.
- \* Accurate measurement of the equilibrium temperature
- \* Displacement of the equilibrium vapour through a delivery tube without condensation.
- \* Collection of the condensable components of the equilibrium vapour
- \* Accurate measurement of the volume of inert gas passed
- \* Chemical Analysis of the components of the phases

Approximately fifty preliminary test runs were made in order to ensure that all the above conditions were attainable.

#### 4.2.1 EQUILIBRATION OF THE LIQUID AND VAPOUR PHASES

The transpiration saturation unit of Halstead and Talbot<sup>(5-6)</sup> was used to equilibrate the liquid phase and vapour phase. The unit was made of jointless glass as shown in Plate 1. An argon gas inlet fed into a five metre coil, so that the argon attained the equilibrium temperature of the silicone oil bath in which the transpiration unit was immersed. The argon gas was led sequentially through three bubbler bottles B1, B2, B3, containing sulphuric acid. This enabled a dynamic equilibrium to be established between the liquid and vapour phases. The maintenance of constant temperature during equilibration was very important. This was achieved by a silicone oil bath, Gallenkamp Model (1031), in which the temperature was controlled to  $\pm 0.2\text{K}$ . The temperature of equilibration was measured with three mercury in glass thermometers, calibrated to  $\pm 0.1\text{K}$  with two placed adjacent to but on opposite sides of the final transpirator bottle. The third thermometer was placed elsewhere in the silicone oil bath. No significant difference in temperature was observed at a particular time between the three thermometers but individual thermometers had a temperature fluctuation of  $\pm 0.2\text{K}$  during experimental runs. The average temperature was taken as the equilibrium temperature.



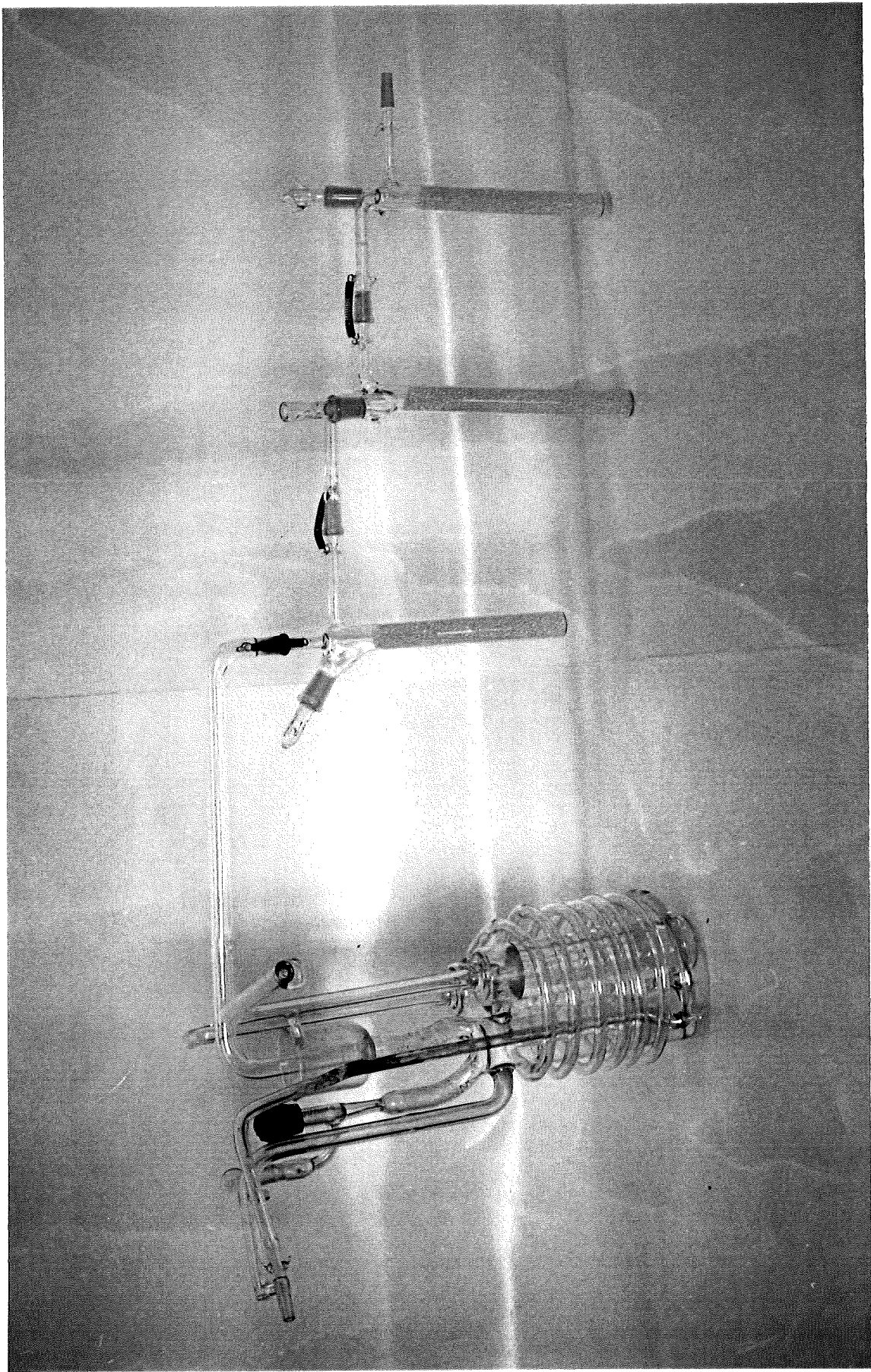


PLATE 1 TRANSPIRATION APPARATUS & COLLECTING BOTTLES

### 4.3.1 COMPARISON OF WATER VAPOUR PRESSURE WITH LITERATURE VALUES

In order to check the suitability of the apparatus for establishing equilibrium conditions, the vapour pressure of pure water at various temperature was determined and compared with literature values. The effectiveness of this approach resides in the fact that the equilibrium vapour pressure values for water are well established.

The results are shown in Table (4.3.1)

(Each experiment was carried at an argon flow rate between 30-40 cc/min)

TEMPERATURE (K)	VAPOUR PRESSURE OF WATER (Pa)	
	EXPERIMENTAL	LITERATURE <sup>(48)</sup>
333.15	$1.86 \times 10^4$	$1.87 \times 10^4$
355.15	$3.20 \times 10^4$	$3.21 \times 10^4$
351.15	$4.13 \times 10^4$	$4.31 \times 10^4$
353.15	$4.52 \times 10^4$	$4.67 \times 10^4$
365.15	$7.44 \times 10^4$	$7.46 \times 10^4$

Table (4.3.1) Experimental and literature water vapour pressure.

The agreement shown in Table (4.3.1) confirms the establishment of equilibrium in the transpiration unit. The slight differences may be attributed to experimental errors introduced as a result of the flow meter used to measure the volume of inert gas passed. This was improved later as reported in section (4.7.1).

#### **4.4.1 FLOW RATE RANGE FOR THE ESTABLISHMENT OF EQUILIBRIUM**

With any transpirator design it is essential to establish the range of flow rates within which equilibrium is established. Halstead and Talbot <sup>(5)</sup> claimed that the flow rate range of 20-60 cc min<sup>-1</sup> was suitable for this transpirator unit. The results below confirm that over the range 20 -60 cc min<sup>-1</sup>, flow rate had no effect on the determined P<sub>H2O</sub> and P<sub>H2SO4</sub> values. Each flow rate range was tested three times and the average value is shown in Table (4.4.1). This shows, at a fixed temperature, the variation of P<sub>H2O</sub> and P<sub>H2SO4</sub> with flow rate. This confirms that the partial pressure is independent of flow rate between 25-55 cc min<sup>-1</sup>. For all subsequent experiments, flow rates were maintained in the range of 30-40 cc min<sup>-1</sup>

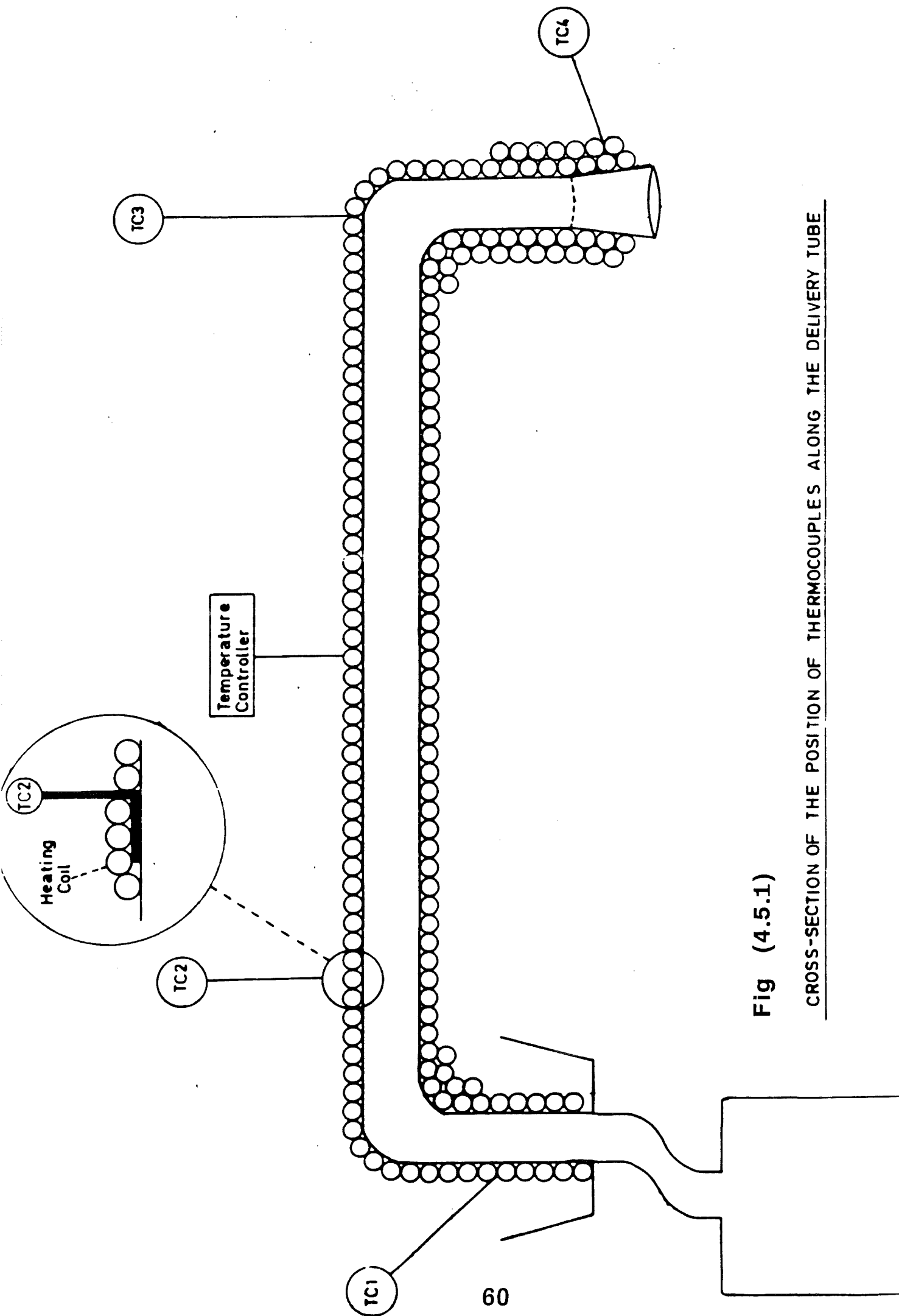
Flow Rate Range (cc min <sup>-1</sup> )	P <sub>H2O</sub> (kPa)	P <sub>H2SO4</sub> (Pa)
20 - 30	7.11	20.16
30 - 40	7.09	18.42
40 - 50	7.09	19.94
50 - 60	6.89	20.12
60 - 70	6.49	17.76
90 - 100	6.21	15.21

Table (4.4.1) Relationship with partial pressure and flow rate.

The above results show a flowrate range; it was not possible to be more precise due to oscillation of the float within the variable area flow meter caused by the bubbling in bottles B1, B2 and B3.

#### **4.5.1 TEMPERATURE CONTROL OF THE DELIVERY TUBE**

It was important to prevent any vapour condensation in the delivery tube. Thus the temperature of the delivery tube must be maintained above the dewpoint temperature. A heating coil powered by a Eurotherm proportional temperature controller model 1C1 was used to maintain the temperature in the delivery tube above the dewpoint. The delivery tube was further insulated by an extra covering of glasswool. The temperature was monitored along the delivery tube with five Cr/Al thermocouples sited as shown in fig (4.5.1). The first thermocouple (TC1) monitored the temperature just above the oil bath oil level at the inlet of delivery tube. The second thermocouple (TC2) monitored the temperature at the position shown in Fig (4.5.1). The middle thermocouple was connected to the temperature controller. The fourth thermocouple (TC3) monitored the temperature at the second bend of the delivery tube where there was a heating coil overlap. The fifth thermocouple (TC4) monitored the temperature near to the out-



**Fig (4.5.1)**

**CROSS-SECTION OF THE POSITION OF THERMOCOUPLES ALONG THE DELIVERY TUBE**

TEMP. BATH (C)	TC 1 (C)	TC 2 (C)	TEMP. CONTROLLER (C)	TC 3 (C)	TC 4 (C)	P <sub>H<sub>2</sub>SO<sub>4</sub></sub> (Pa)	P <sub>H<sub>2</sub>O</sub> (kPa)
165	170	170	180	170	200	8.16	12.90
165	175	210	210	230	300	22.60	12.81
165	180	200	200	220	250	6.67	13.56
165	185	185	200	195	210	6.26	13.03
165	190	220	220	240	270	21.69	14.06
165	190	190	200	225	300	22.27	13.48
165	200	200	200	210	250	28.86	12.99
165	210	210	200	210	210	25.27	13.09
165	210	220	220	250	300	27.32	13.00
165	220	220	220	220	250	26.88	13.38
165	220	220	220	250	300	26.77	13.42
165	220	220	220	250	300	27.28	14.01

Table (4.5.1) Delivery tube temperature analysis

let of the tube where the condenser bottle was connected. Due to the high thickness of glass at this place, the temperature was maintained higher than elsewhere.

Table (4.5.1) shows that consistent results, particularly for  $\text{PH}_2\text{SO}_4$  were only obtained if the temperatures recorded by the thermocouples were at least  $35^\circ\text{C}$  higher than the silicone oil bath temperature. This condition was maintained for all the experiments.

#### **4.6.1      COLLECTION OF THE CONDENSABLE COMPONENTS**

The collecting arrangements of Halstead and Talbot employed ice/water and  $\text{CO}_2/\text{Acetone}$  as coolants for the first and final collecting bottles respectively. The first modification introduced in the present work was that extra collecting bottles were fitted as shown in Fig (4.6.1) and the replacement of  $\text{CO}_2/\text{Acetone}$  by *n*-propanol cooled with liquid nitrogen, which maintain a temperature  $-100^\circ$  to  $-120^\circ\text{C}$  as opposed to  $-79^\circ\text{C}$  for  $\text{CO}_2/\text{Acetone}$ . Additionally, glass beads were introduced into the first three bottles to increase the cooling surface area. The design allowed the withdrawal of the glass beads through a cone for titration purposes. The dimensions of the collecting bottles are shown in Fig (4.6.2). Further traps containing very dilute alkali and water at ambient temperature and an indicator

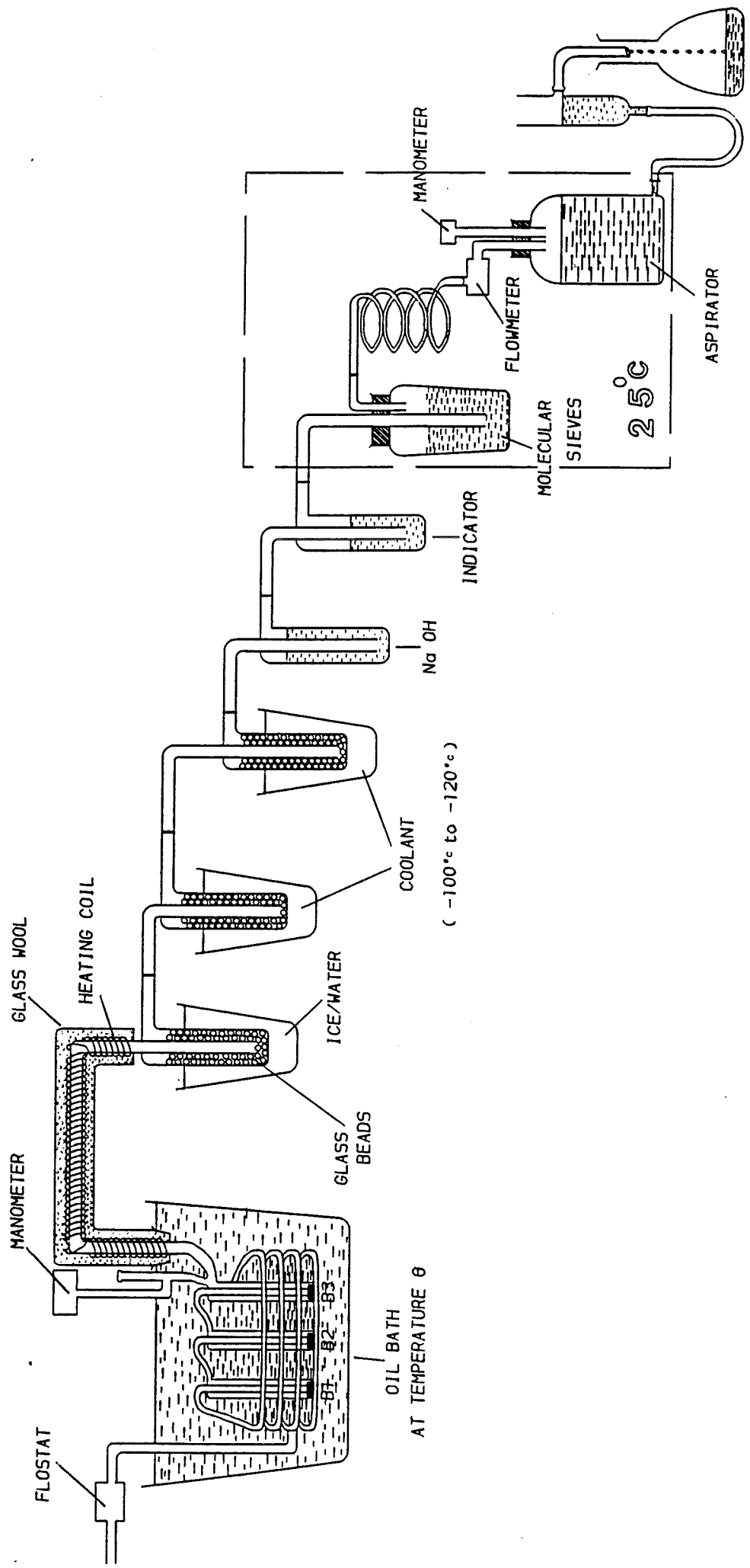


Fig. (4.6.1) TRANSPIRATION APPARATUS



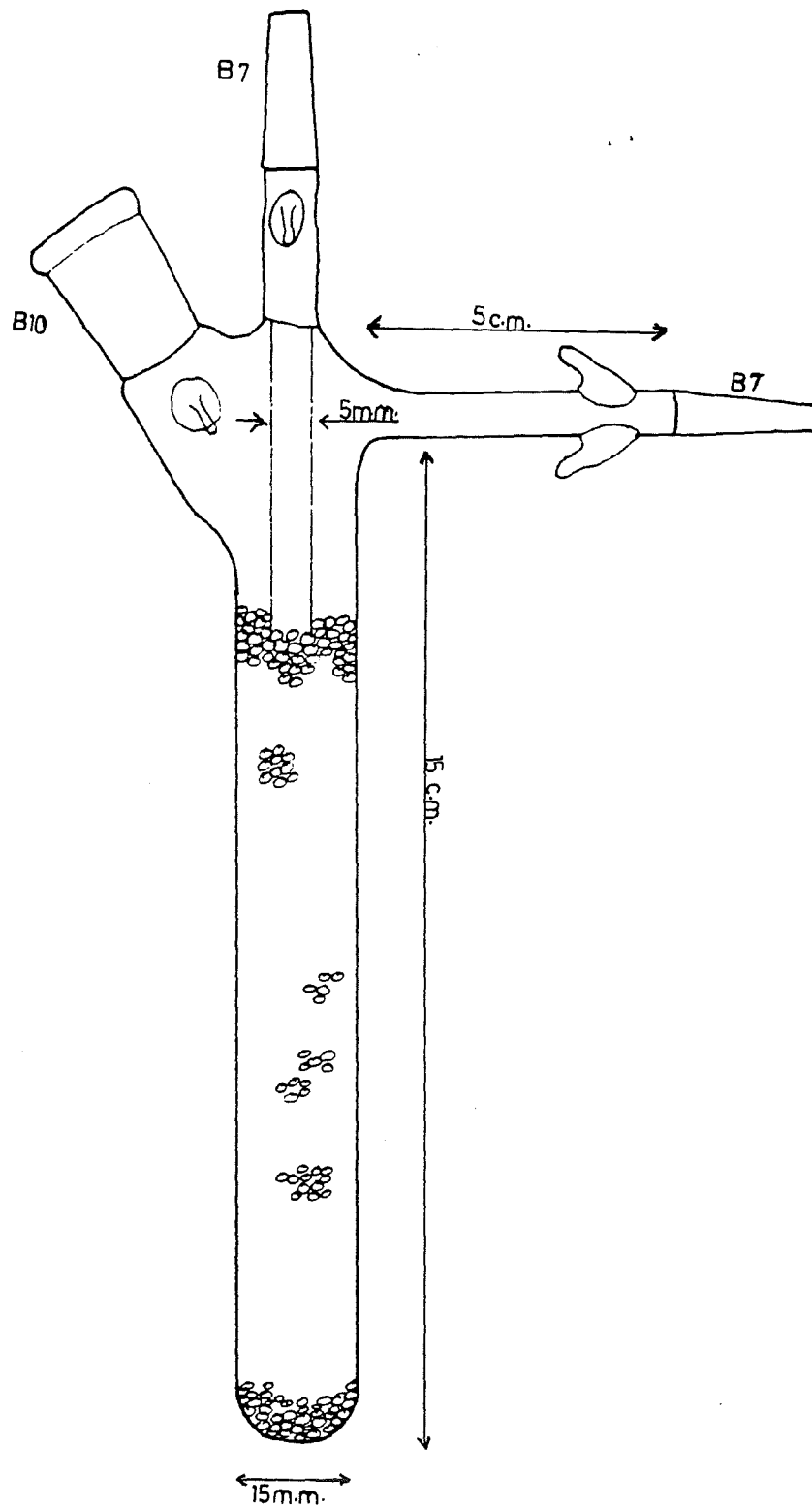


Fig (4.6.2) VAPOUR TRAP

for acid were also added to the system as shown in Fig (4.6.1) to confirm that no acidic vapours escaped collection in the upstream vessels.

In the absence of the 4th and 5th bottles it was found that 85%, 14%, 1%, w/w of the condensate was collected in the first, second and third bottles respectively. However with the 4th & 5th bottles added 92%, 7%, 1%, w/w was collected in the first, second and third bottles respectively. It is assumed that the periodic restriction and surge in the gas stream as the bubbles form and are released in the fourth trap, aids convection to the cooled surface in the upstream condensers.

This collecting system was found to be very effective and the scrubber used by Halstead and Talbot<sup>(5)</sup> to recover the last traces of H<sub>2</sub>SO<sub>4</sub> was therefore unnecessary. A scrubber is regarded as undesirable as it would not detect any water vapour associated with the sulphuric acid.

#### 4.7.1 MEASUREMENT OF THE VOLUME OF INERT GAS

The volume of inert gas passed in an equilibration run was important in determining the partial pressure of each component. In Halstead and Talbot's<sup>(5-6)</sup> work a variable area type flow

meter, type KD9, model 1100 was used to measure the volume of inert gas passed. A data leaflet for the KD9 flowmeters showed an accuracy of only  $\pm 4\%$  for the flowmeter. In addition there was oscillation of the float due to the bubbling which takes place in the system. In view of these difficulties an alternative method of measuring the total gas volume was developed as shown in Fig (4.6.1). At the downstream end of the train, argon was allowed to displace water from an aspirator. The displaced water, which was equal to the total volume of argon pumped, was then collected in a large volumetric flask. The run was stopped when a volume of 5 to 10 litres, depending in the run, was collected in the volumetric flask. The arrangement shown in Plate 2 allowed the argon collecting in the aspirator to be maintained at atmospheric pressure. The aspirator was held in a thermostatically controlled box which was maintained at  $25^{\circ}\text{C}$  with a control unit. The incorporation of a 3 metre long glass coil inside this box allowed the gas to be delivered to the aspirator at  $25^{\circ}\text{C}$ . The flowmeter positioned between the coil and aspirator was merely included for guidance.

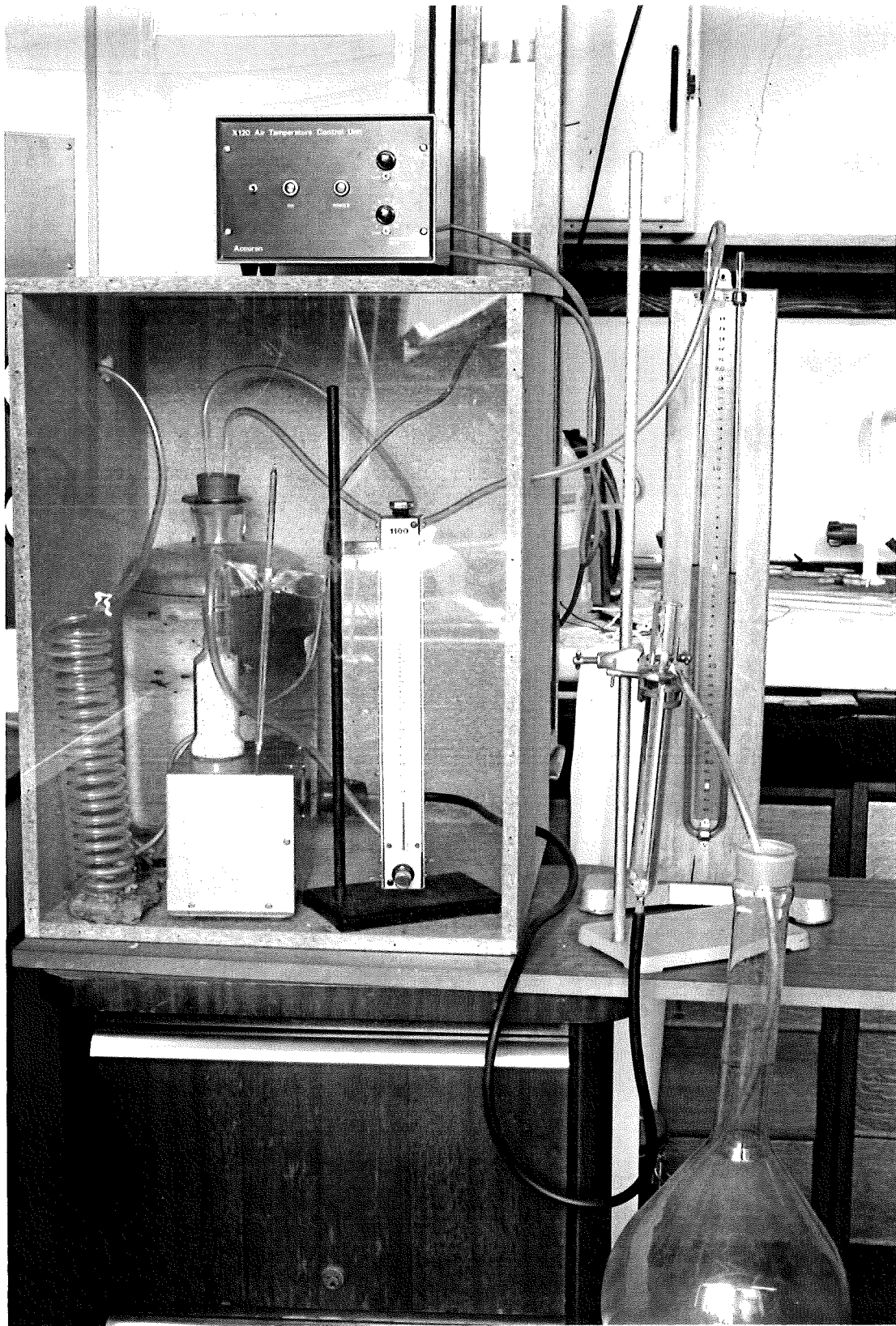


PLATE 2 VOLUME MEASURING UNIT

## **4.7.2 MEASUREMENT OF EQUILIBRIUM PRESSURE**

A knowledge of the absolute pressure of the equilibrated vapour phase is necessary. This was determined at the exit of the third transpiration bottle with a detachable paraffin manometer -

( $\rho = 0.784$ ) with an accuracy  $\pm 1$  mm H<sub>2</sub>O via a greaseless tap connected by capillary tubing. The atmospheric pressure was determined to  $\pm 0.05$  mm Hg by a Fortin barometer. Both pressures were combined to determine the absolute total pressure of the vapour phase.

## **4.8.1 ANALYSIS OF THE CONCENTRATED H<sub>2</sub>SO<sub>4</sub> USED IN THE TRANSPIRATOR**

"Analar" 98.9 w/w% acid was diluted to 75-90 w/w% strength for use in the transpirator bubblers. The precise acid concentration used was determined by dispensing a known weight of the solution from a weight pipette into a 500 cc volumetric flask, making upto the mark, and titrating with standard "Analar" 1 molar NaOH solution using methyl orange indicator.

#### **4.9.1 DETERMINATION OF THE AMOUNTS OF CONDENSABLE COMPONENTS**

The condensed acidic vapours collected in the bottles were first weighed on a Sartorius 1773 type balance to an accuracy of 0.1 mg. The acids collected and the beads were then transferred into a conical flask and the bottles were washed with distilled water. The acid content was then titrated against NaOH BDH analytical volumetric solution using BDH '4460' indicator.

#### **4.10.1 PROCEDURE FOR H<sub>2</sub>O/H<sub>2</sub>SO<sub>4</sub> RUNS**

A known concentration (75 - 90 % w/w ) sulphuric acid was introduced into the bubblers B1, B2, and B3. The transpiration unit was then placed into the oil bath and brought to the required temperature. At the same time the delivery tube heating coil was switched on. Meanwhile the first three collector bottles were weighed connected together and kept in the coolant. The NaOH bottle, indicator bottle and the aspirator were then connected to the upstream collector bottles.

Argon gas (BOC Zero) from a cylinder was allowed to enter the 5 metre coil through a steady flow controller 'flostaf' and passed through bubblers B1, B2, B3 at a rate of 30 - 40 cc min<sup>-1</sup>. After allowing 15 - 30 minutes for equilibrium to be established, the collecting bottle assembly was connected to the delivery tube. Collection of the equilibrium vapours in the coolant bottles, and the inert gas in the aspirator then commenced as shown in Plate 3. The experiment was stopped when the water level reach the top level mark of the volumetric flask, by disconnection of the delivery tube. The collector bottles were then separated, closed with lids, weighed and their contents analysed.

#### **4.11.1 PROCEDURE FOR H<sub>2</sub>O/H<sub>2</sub>SO<sub>4</sub>/HCl RUNS**

The procedure was identical to that used for the H<sub>2</sub>O/H<sub>2</sub>SO<sub>4</sub> system except that HCl was introduced as a constant volume mixture from a Ar/HCl cylinder. The HCl/Ar mixtures were specially prepared for this work by the British Oxygen Company and a certificate of analysis was given for each cylinder. Two mixtures were used; one containing a constant mixture of argon with 1010 vpm HCl, the

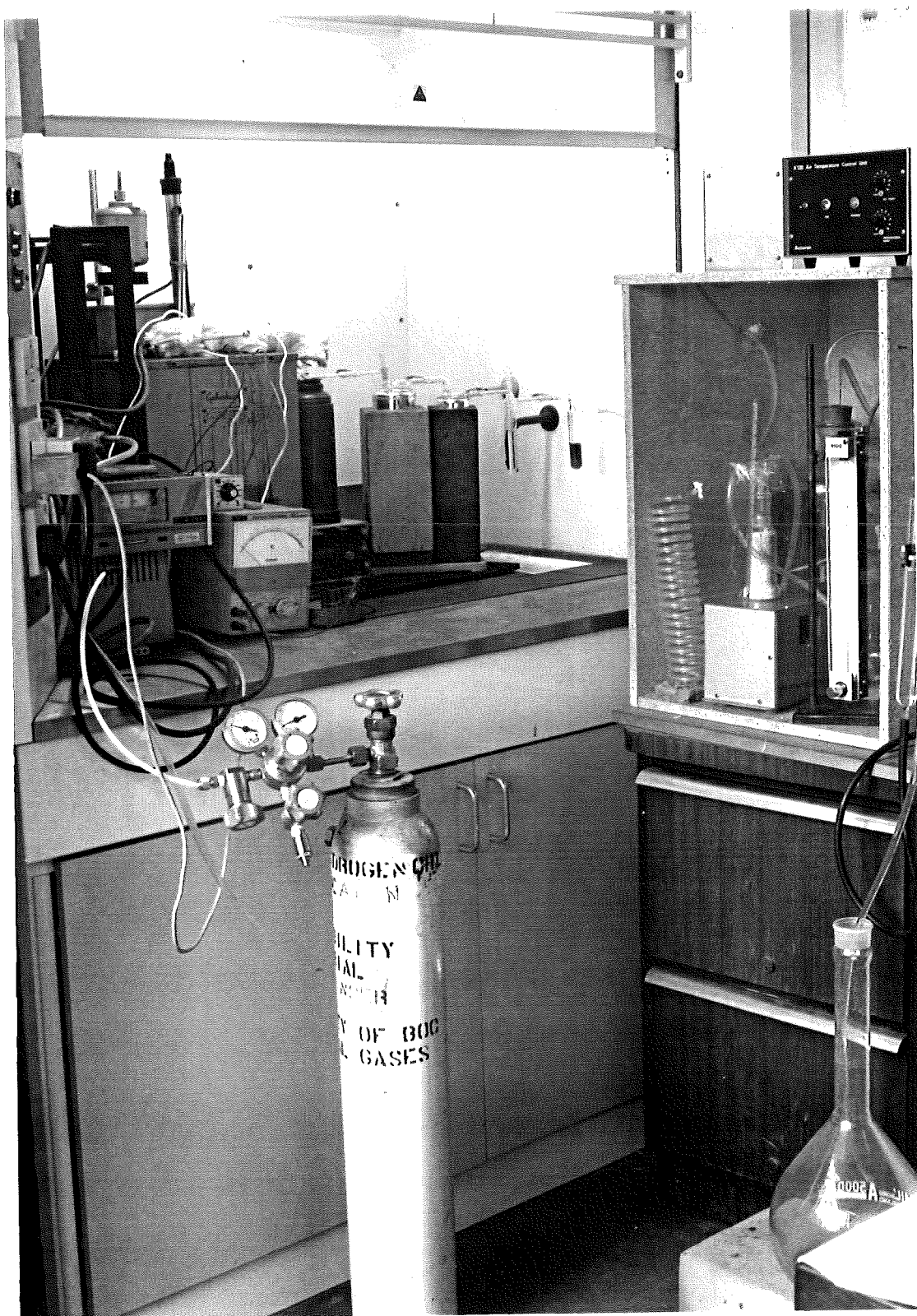


PLATE 3 GENERAL APPEARANCE OF THE UNIT

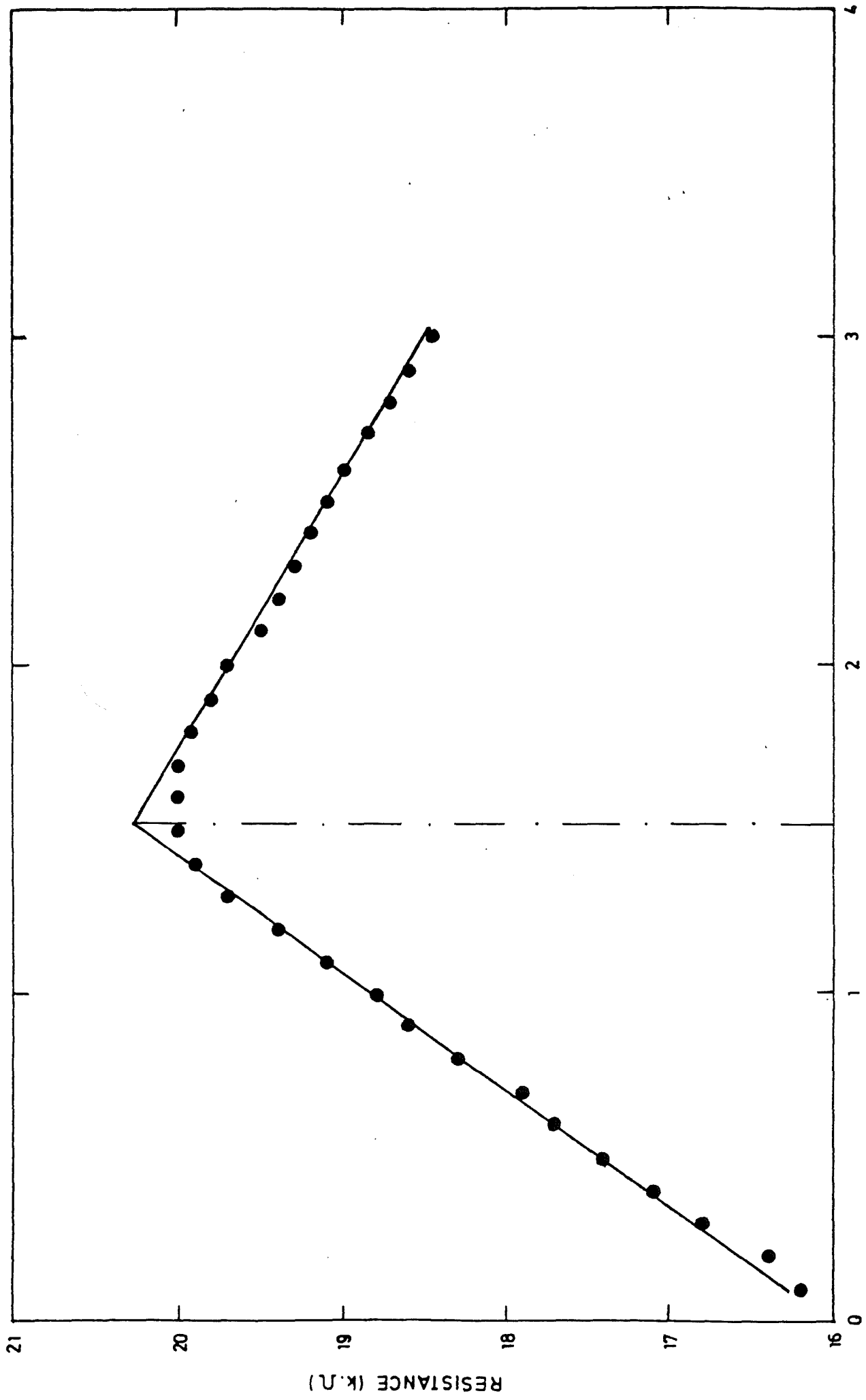


other cylinder was a constant mixture of argon with 528 ppm HCl.

At various stages during the life of the HCl/Ar cylinders, the gas compositions were checked. A known volume (5 - 10 litres) of gas was passed through two bottles of water and the amount of acid collected was determined. No significant change in composition was detected.

#### **4.11.2 THE ANALYSIS OF H<sub>2</sub>O/H<sub>2</sub>SO<sub>4</sub>/HCl RUNS**

The approach was the same as that used for the H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O system. The vapours, including HCl, were again effectively collected in the first three bottles. The water and total acid content were analysed by weight and titration as for the H<sub>2</sub>O/H<sub>2</sub>SO<sub>4</sub> system and the HCl content was separately determined using a conductimetric procedure against a AgNO<sub>3</sub> solution. Fig (4.11.1) shows a typical plot.



Fig(4.11.1) A typical plot for  $Cl^-$  analysis using conductometric titration

## **5.0 RESULTS AND ANALYSIS**

### **5.1.1 INTRODUCTION**

In total fifty seven experimental runs were carried out. These were performed with argon only, argon + 528 vpm HCl and argon + 1010 vpm HCl gases. The sulphuric acid in the transpirators was used in three different concentrations of sulphuric acid mole fraction 0.475, 0.492 and 0.515 respectively. The experiments were carried out at temperatures of 140°, 150°, 160°, 165°, and 175° C.

The experimental results are given in Tables 5.1.1, 5.1.2 and 5.1.3 . Column 4 gives the concentration of HCl used during the experiment in vpm. Calculations of the partial pressure are shown in appendix 1.

### **5.2.1 HCl EFFECT ON DEWPOINTS**

Tables 5.1.1, 5.1.2 & 5.1.3 show that the vapour pressures of H<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub> were not affected by the presence or absence of HCl in the system. Further more the enthalpy of vaporisation of sulphuric acid ( $\Delta H_{H_2SO_4}$ ) calculations show that

X MOLE fraction [H <sub>2</sub> SO <sub>4</sub> ]	T (C)	T (K)	HCl (vp m)	P <sub>H<sub>2</sub>O</sub> (kPa)	P <sub>H<sub>2</sub>SO<sub>4</sub></sub> (Pa)	Δ H (kJ/mol)
0.475	155	428.2	0	10.73	12.82	79.31
0.475	155	428.2	0	10.62	12.78	79.32
0.475	155	428.2	528	10.65	12.07	79.52
0.475	155	428.2	528	10.64	11.93	79.56
0.475	155	428.2	528	10.52	13.72	79.07
0.475	155	428.2	1010	10.75	12.91	79.28
0.475	155	428.2	1010	10.57	13.28	79.18
0.475	160	433.2	0	12.77	17.57	79.11
0.475	160	433.2	0	12.73	17.60	79.11
0.475	160	433.2	0	12.61	17.93	79.04
0.475	160	433.2	528	13.06	17.11	79.23
0.475	160	433.2	528	12.73	16.85	79.27
0.475	160	433.2	528	12.81	17.31	79.17
0.475	160	433.2	1010	13.24	15.46	79.57
0.475	160	433.2	1010	12.82	15.46	79.58
0.475	160	433.2	1010	12.58	16.30	79.39
0.475	165	438.2	0	15.59	19.75	79.61
0.475	165	438.2	0	15.38	20.59	79.46
0.475	165	438.2	528	15.48	19.35	79.69
0.475	165	438.2	528	14.95	18.61	79.83

0.475	165	438.2	528	14.52	20.20	79.53
0.475	165	438.2	1010	14.89	21.55	79.30
0.475	165	438.2	1010	14.47	22.63	79.12
0.475	175	448.2	0	18.28	30.22	79.86
0.475	175	448.2	0	17.97	30.34	79.85
0.475	175	448.2	1010	18.15	29.66	79.93
0.475	175	448.2	1010	17.03	32.13	79.63

Table (5.1.1) Partial pressure and enthalpy of vaporisation calculated from the experimental data for sulphuric acid concentration 0.475 mol.

X MOLE fraction [H <sub>2</sub> SO <sub>4</sub> ]	T (C)	T (K)	HCl (vp m)	P <sub>H<sub>2</sub>O</sub> (kPa)	P <sub>H<sub>2</sub>SO<sub>4</sub></sub> (Pa)	Δ H (kJ/mol)
0.492	165	438.2	0	12.99	28.86	79.13
0.492	165	438.2	0	13.09	25.27	79.61
0.492	165	438.2	0	13.00	27.32	79.33
0.492	165	438.2	0	13.42	26.77	79.41
0.492	165	438.2	0	14.01	27.28	79.34
0.492	165	438.2	0	13.38	26.88	79.39
0.492	165	438.2	528	12.68	27.44	79.31
0.492	165	438.2	528	12.58	28.30	79.20

Table (5.1.2) Partial pressure and enthalpy of vaporisation calculated from the experimental data for sulphuric acid concentration 0.492 mol.

X MOLE	T	T	HCl	P <sub>H2O</sub>	P <sub>H2SO4</sub>	$\Delta H$
fraction [H2SO4]	(C)	(K)	(vp m)	(kPa)	(Pa)	(kJ/mol)
0.515	140	413.2	0	3.77	6.58	80.47
0.515	140	413.2	0	3.91	6.72	80.40
0.515	140	413.2	0	3.79	8.25	79.69
0.515	140	413.2	528	3.73	5.87	80.86
0.515	140	413.2	1010	3.76	6.46	80.53
0.515	155	428.2	0	6.67	20.16	79.48
0.515	155	428.2	0	6.78	18.42	79.80
0.515	155	428.2	0	6.79	19.94	79.52
0.515	155	428.2	0	6.77	20.12	79.49
0.515	155	428.2	528	6.89	16.23	80.25
0.515	155	428.2	1010	7.11	18.18	79.85
0.515	155	428.2	1010	7.09	19.55	79.59
0.515	155	428.2	1010	7.09	18.89	79.71
0.515	160	433.2	0	7.96	21.22	80.25
0.515	160	433.2	0	8.10	20.49	80.37
0.515	160	433.2	1010	7.94	21.25	80.24
0.515	165	438.2	0	9.76	31.79	79.72
0.515	165	438.2	0	9.74	31.18	79.79
0.515	165	438.2	0	9.61	31.83	79.72
0.515	165	438.2	528	9.80	28.72	80.09
0.515	165	438.2	1010	9.71	24.42	80.68
0.515	165	438.2	1010	9.95	31.62	79.74

Table (5.1.3) Partial pressure and enthalpy of vaporisation calculated from the experimental data for sulphric acid concentration 0.515 mol.

there is hardly any different in the enthalpy of vaporisation of sulphuric acid values with or without HCl in the argon gas. It was also found that all the gaseous HCl passed with the argon through the concentrated sulphuric acid in the transpirators and was collected in the condensing bottles. This was further confirmed by establishing that no chloride at all could be detected in the concentrated sulphuric acid removed from the transpirators at the finish of the experimental runs with argon + HCl gas mixtures.

## 5.2.2 HCl EFFECT ON THE CALCULATED VAPORISATION ENTHALPY

Values for the enthalpy change for vapourisation of sulphuric acid were calculated from the experimental results and are shown in Tables 5.1.1, 5.1.2 and 5.1.3. The calculations of  $\Delta H_{H_2SO_4}$  are shown in appendix 2.

The experimental results for argon only and argon with HCl are compared below in Table 5.2.1.

	$H_{H_2SO_4}$ (kJ mol <sup>-1</sup> )	No of Estimates	Estimate of S.D.
Argon only	79.61	27	0.40
Argon + HCl	79.66	30	0.47



Table (5.2.1) Comparison of vapourisation enthalpy of sulphuric acid with and without HCl.

These results further confirm that there is hardly any difference between the experiments carried out with and without HCl gas.

### **5.3.1 SOLUBILITY OF HCl (aq) IN CONCENTRATED H<sub>2</sub>SO<sub>4</sub>**

A small amount of concentrated HCl (approximately 35% w/w) was added to two separate beakers containing 100 ml of concentrated H<sub>2</sub>SO<sub>4</sub> (approximately 75 to 90%) maintained respectively at room temperature and at 150°C. In both cases a vigorous reaction ensued and gaseous HCl was liberated. Analysis with AgNO<sub>3</sub> solution showed no detectable presence of HCl in the liquid system at 150°C. This experiment was repeated at different temperatures (between room temperature and 150°C) and indicated only a very slight chloride solubility in sulphuric acid at temperatures below 50°C.

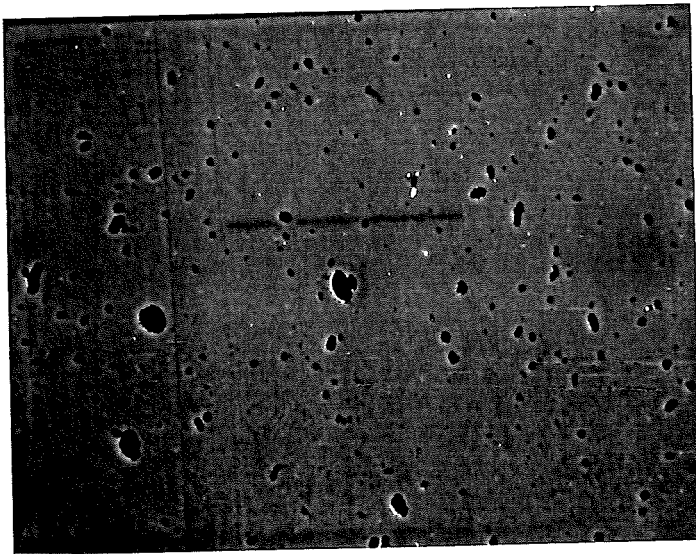
This is thus in accord with the room temperature finding of Luchinskii and Likhacheva<sup>(26)</sup> as shown in section (2.3.2).

It seems evident that concentrated  $\text{H}_2\text{SO}_4$  is able to dehydrate  $\text{HCl}$  (aq) and thus remove its solution sheath owing to  $\text{H}_2\text{SO}_4$ 's greater affinity for water molecules.

The importance of this finding for this work, which was carried at high temperature, is that  $\text{HCl}$  is effectively insoluble over the concentration and temperature range investigated and thus behaves merely as an inert gas.

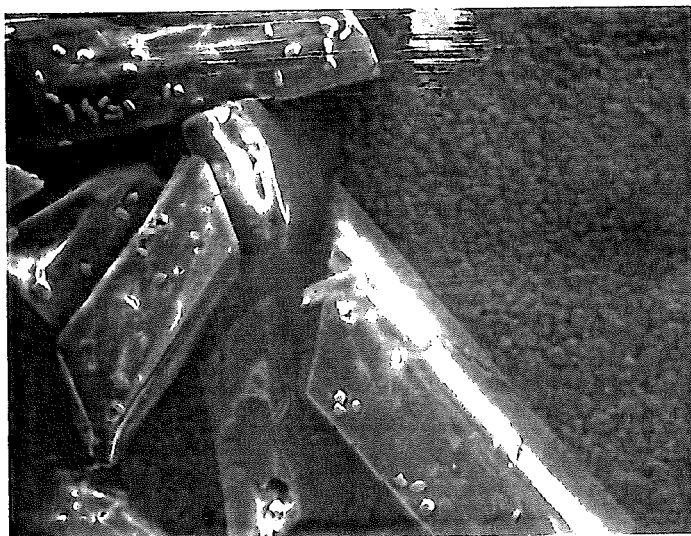
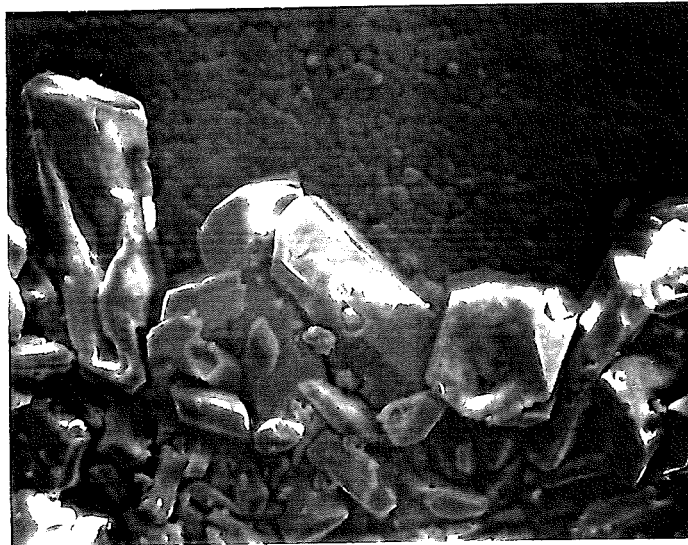
#### **5.4.1 INFLUENCE OF HCL ON MILD STEEL STUDIED BY SCANNING ELECTRON MICROSCOPY (SEM) AND X RAY ENERGY DISPERSIVE ANALYSIS (EDAX)**

The small piece of mild steel was introduced into the third transpiration bottle containing the equilibrium vapour in the  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  system. Similarly another piece was placed in the  $\text{HCl}/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  system. After approximately one hour in the equilibrium vapours the metal pieces were removed, allowed to dry in a desiccator and examined for corrosion products using SEM/EDAX. The SEM photographs and the EDAX elemental analysis, as shown in fig (5.4.1) and fig (5.4.2-4), revealed the same corrosion products for both systems. Specifically the crystalline materials identified in the photographs contain a high proportion of sulphate as expected from corrosion involving  $\text{H}_2\text{SO}_4$ . More significantly however there was no indication of any chloride in the corrosion products.



**Polished Surface**

**After  
 $H_2SO_4$   
corrosion**

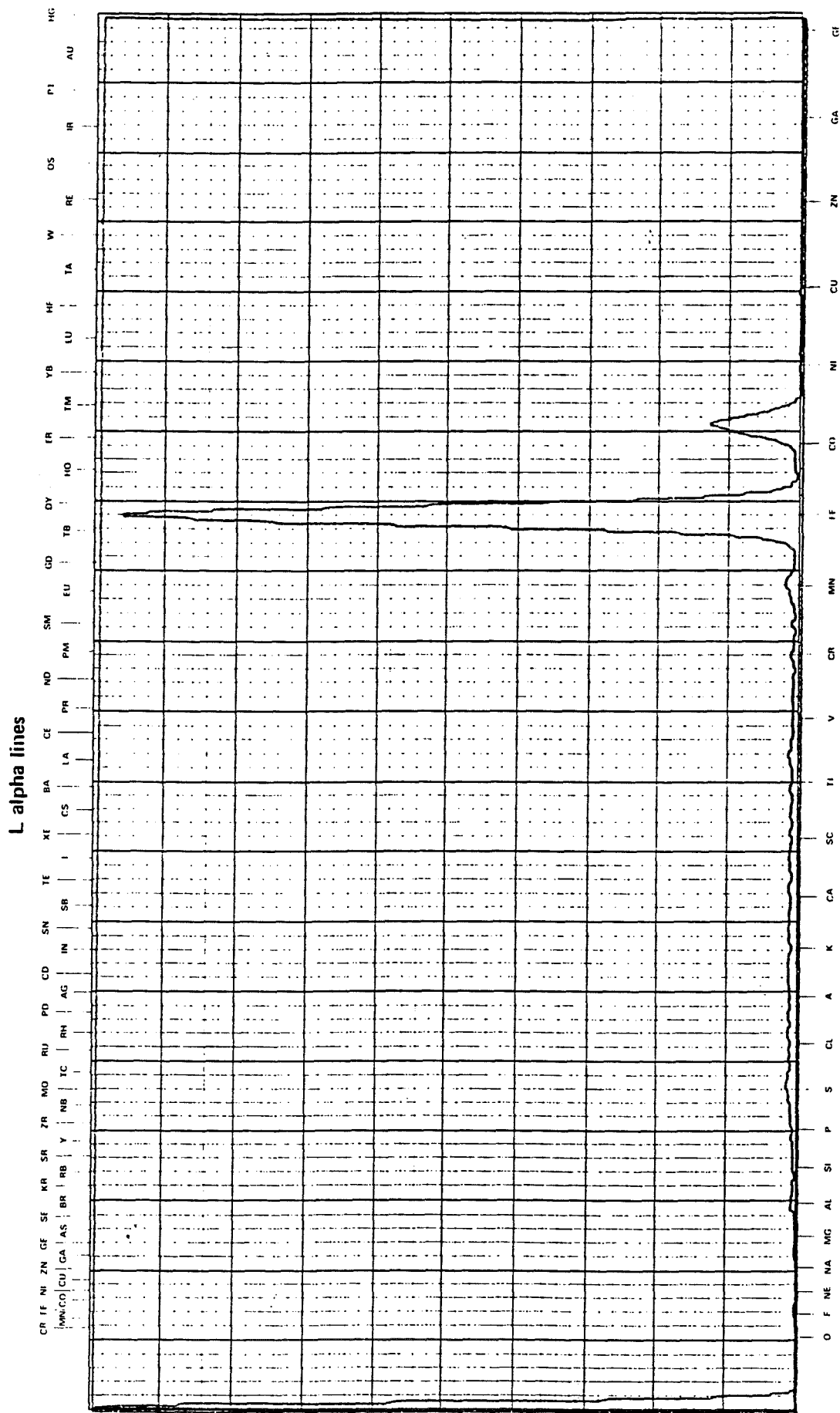


**After  
 $H_2SO_4/HCl$   
corrosion**

**Fig (5.4.1) Scanning electron microscopy  
Photographs of corrosion products**

Laboratory.....  
 Sample..... *S4 Mild steel, 1 micron polished*  
 Researcher..... *A. L. S. Vasanth Kumar*  
 Date..... *10/2/87*

KeV.....  
 Seconds.....  
 Take off Angle.....



**Fig (5.4.2) EDAX Analysis on polished surface**

Laboratory.....  
 Sample S6 Mild steel after exposure to H<sub>2</sub>O/H<sub>2</sub>SO<sub>4</sub> why  
 Researcher... ALS Vasanthakumari  
 Date..... 10/2/87

KeV.....  
 Seconds.....  
 Take off Angle.....

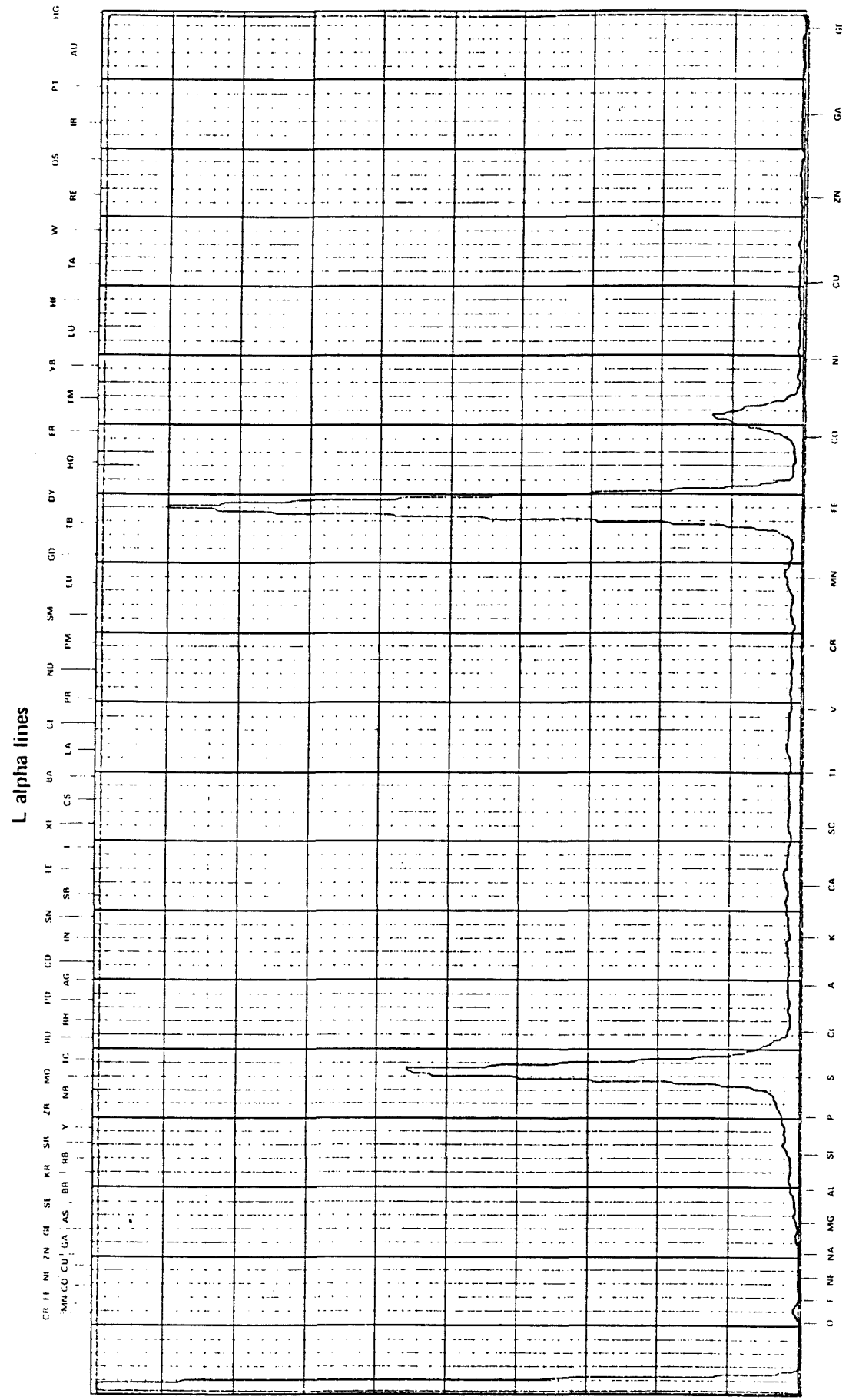


Fig (5.4.3) EDAX Analysis on H<sub>2</sub>SO<sub>4</sub> corrosion

Laboratory.....

Researcher... *ALS Vasanthakumar*

Date... *10/2/87*

Sample... *57*

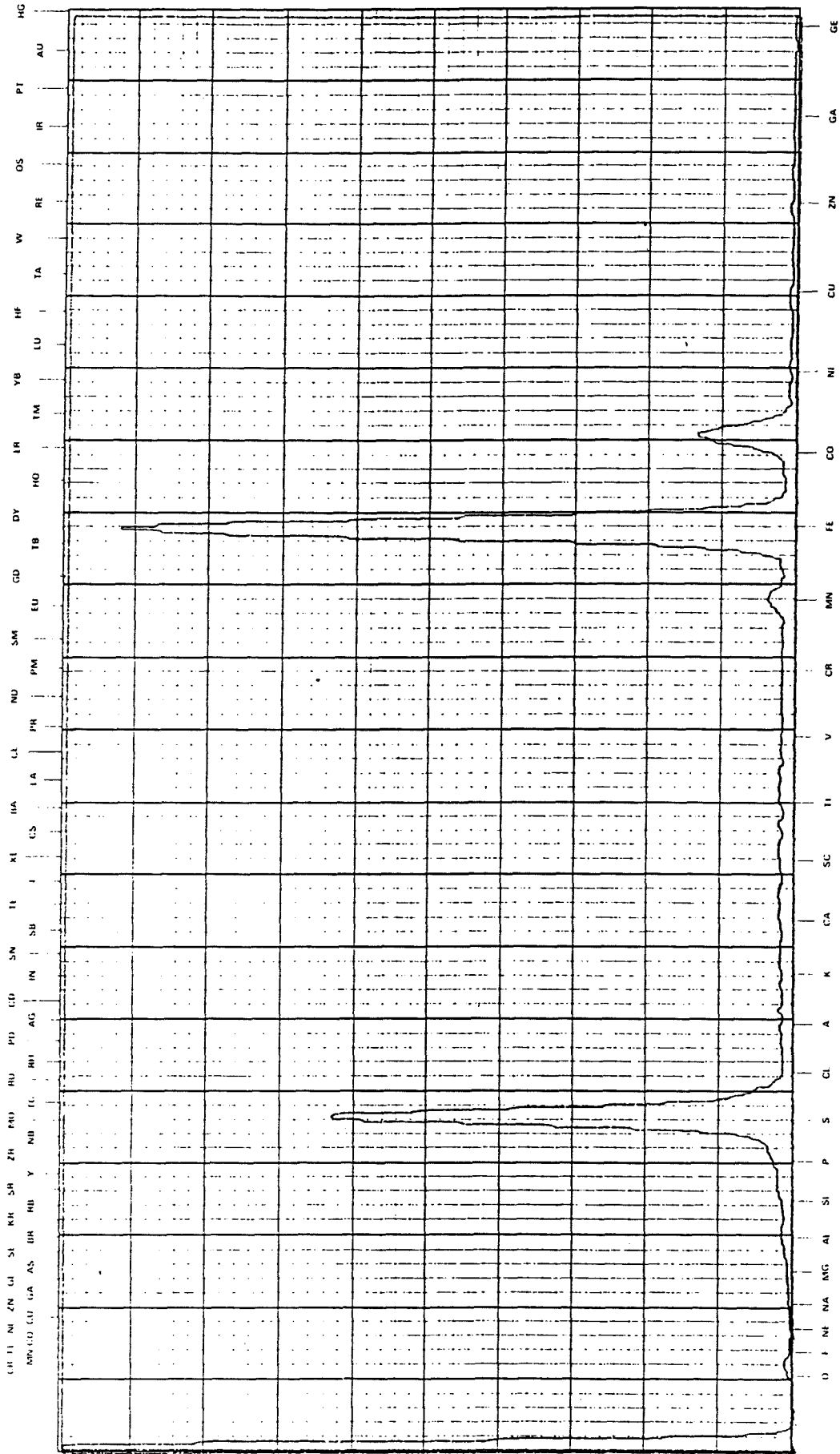
*Mild steel after exposure to H<sub>2</sub>O/H<sub>2</sub>SO<sub>4</sub>/HCl*

KeV.....

Seconds.....

Take off Angle.....

L alpha lines



K alpha lines

Fig (5.4.4) EDAX Analysis on HCl/H<sub>2</sub>SO<sub>4</sub> corrosion

This finding confirms chlorine insolubility and dewpoint independence findings. It is also in accord with the Meadowcroft and Cox's <sup>(7)</sup> finding that HCl in the flue gas stream had no effect on metal corrosion rates above 70°C.

## **5.5.1 DISCUSSION**

The dewpoint temperature can be calculated if precise thermodynamic data for H<sub>2</sub>SO<sub>4</sub> is available. However the precision is limited owing to the uncertainty in the value of  $\Delta H_{H_2SO_4}$ .

An analysis of previous work has established that the precision is limited. This is evident from tables (Appendix 3). An analysis of the data of Haase and Rehse (Appendix 3) has revealed  $\Delta H$  values ranging from 65.83 to 80.65 kJ mol<sup>-1</sup>. Analysis of further data by Haase and Borgman shows  $\Delta H$  ranging from 74.13 to 81.46. kJ mol<sup>-1</sup>

The Haase and Rehse data comprised 83 points covering 44% to 97.5% acid concentration and a temperature range of 57°C to 322°C. However it is not clear whether these workers were aware of H<sub>2</sub>SO<sub>4</sub> dissociating into SO<sub>3</sub> and H<sub>2</sub>O beyond 175°C <sup>(25)</sup>. Additionally, at very low concentrations, typically few particles per million million, it is believed that analytical difficulties exist with respect to the conductrimetry method.

	Present work without HCl	Present work with HCl	Halstead & Talbot	HAASE & REHSE	HAASE & BORGMAN
$\Delta H_{H_2SO_4}$	79.61	79.64	79.2	80.02	80.40
$\sigma_{n-1}$	0.40	0.47	0.35*	0.58	0.72

Table (5.5.1) Summary of the  $\Delta H$  values.

\*The standard deviation figures cited by Halstead and Talbot (0.165 and 0.175) relate to nine values which are themselves averages of four determinations. These values are related to standard deviations from a number of individual determinations by

$$\sigma_{n-1} = \frac{\sigma_{n-1}^*}{\sqrt{n}} \quad \text{with } n = 4$$

This correction has been incorporated in the figures for the tables.



In the later work of Haase and Borgman (Appendix 3) high temperatures above 190°C and low concentrations were avoided. Here, from an analysis of 91 points covering 64% to 80% acid concentrate and 90° - 190°C, the experimental results yield an average for  $\Delta H$  of 78.52kJ/mol. A subsequent analysis of this data by Halstead and Talbot yielded an average value of 78.77kJ/mol. This was achieved by rejecting 6 data points which showed gross deviations from the slope. Halstead and Talbot then combined the remaining 85 points with their nine experimental points and presented a  $\Delta H$  value of 78.8 kJ mol<sup>-1</sup>.

### **5.5.2      COMPARISON OF $\Delta H(H_2SO_4)$ CALCULATED FROM THE EXPERIMENTAL DATA OF VARIOUS INVESTIGATORS**

A comparison was made with the data of Halstead and Talbot, Haase and Borgman and Haase and Rehse.

However Haase et al experiments were only considered within the range of concentration 75-90% w/w and at temperature less than 175°C

Table (5.5.1) shows a summary of the  $\Delta H$  values covering the above mentioned concentration and temperature ranges.

## 5.6.1 CONCLUSIONS

### CONCLUSION 1

The three factors

(1) Partial pressure

(2)  $\Delta H_{H_2SO_4}$  VALUE

(3) Metal corrosion

are not affected by the presence of HCl

This confirms that the dewpoint is not affected by the presence of HCl in flue gases in the range of interest in a power station

### CONCLUSION 2

The  $\Delta H$  value determined from the developments adopted in this work yield a value of  $79.6 \text{ kJ mol}^{-1}$ . This results from the greater accuracy of the experimental method and the number of results analysed.

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# **APPENDIX**

## **APPENDIX 1**

**Calculation of Partial Pressure**

## **APPENDIX 2**

**(1) Computer programme for calculation of**

**$\Delta H_{H_2SO_4}$**

**(11) Computer programme for calculation of partial Pressure**

## **APPENDIX 3**

**HAASE & BORGMANN and HAASE & REHSE**

**$\Delta H_{H_2SO_4}$  values**

## APPENDIX 1

A typical calculations of partial pressures from experimental reading is given below. It is based on one of the three experiments carried out for a sulphuric acid concentration of 0.492 mol and at an equilibrium temperature of 165 C.

	weight start (g)	weight finish (g)	collected amount of acid weight (g)
collecting bottle (1)	55.6853	56.4392	0.7539
collecting bottle (2)	65.7705	65.8370	0.0665
collecting bottle (3)	51.6488	51.6568	0.0080

collected amount of Argon 7 litres at 25 C

Equilibrium pressure = 155 mm H<sub>2</sub>O

Atmospheric pressure = 750.3 mm Hg

Experiment Temperature 165 C

Using  $PV = nR_0T$  Number of moles of Argon  $n_{Ar}$

$$(750.3/750) * 10^5 * (7/1000) = n_{Ar} * 8.3144 * 298.2$$

$$n_{Ar} = 0.2824$$

collected amount of sulphuric acid  $n_{\text{H}_2\text{SO}_4}$

Required amount of 0.01 (m) NaOH = 17.6 cc

$n_{\text{H}_2\text{SO}_4} = 17.6 \cdot (0.1/2000)$  -----  $n_{\text{H}_2\text{SO}_4} = 8.8 \cdot 10^{-5}$

Weight of sulphuric acid =  $8.6 \cdot 10^{-3}$  g

Weight of water = 0.8138 g

$n_{\text{H}_2\text{O}} = 0.0452$

Total moles = 0.3276

Total Pressure at the equilibrium =  $(761.7/750) \cdot 10^5$  Pa

Partial Pressure of  $\text{H}_2\text{SO}_4$  = 27.28 Pa

Partial Pressure of  $\text{H}_2\text{O}$  = 14.01 kPa

## APPENDIX 2

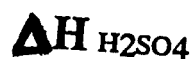
(1) Computer programme for the calculation of  $\Delta H_{\text{H}_2\text{SO}_4}$

(11) Computer programme for the calculation of partial pressures

The Programme is written using the thermodynamic equation derived in Chapter 2 for the calculation of partial pressure. , The required thermodynamical values are taken from published data as discussed in Chapter 3 and Chapter 5.



## Computer programme for the calculation of



```
100 N = 22
110 DIM X(N), A(N)
115 DIM B(N), C(N), D(N)
120 X(1) = .444: A(1) = 6.25
121 X(3) = .465: A(3) = - 11.38
122 X(2) = .454: A(2) = - 2.05
123 X(4) = .476: A(4) = - 21.84
124 X(5) = .488: A(5) = - 32.68
125 X(6) = .494: A(6) = - 35.50
126 X(7) = .5: A(7) = - 36.86
127 X(8) = .506: A(8) = - 35.5
128 X(9) = .512: A(9) = - 33.26
129 X(10) = .520: A(10) = - 25.5
130 X(11) = .526: A(11) = - 17.03

131 X(12) = .533: A(12) = - 7.5
132 X(13) = .54: A(13) = - .62
133 X(14) = .547: A(14) = 4.75
134 X(15) = .555: A(15) = 9.2
135 X(16) = .571: A(16) = 14.52
136 X(17) = .588: A(17) = 17.70
137 X(18) = .606: A(18) = 20.04
138 X(19) = .625: A(19) = 21.5
139 X(20) = .645: A(20) = 22.51
140 X(21) = .666: A(21) = 23.09
141 X(22) = .690: A(22) = 23.43
142 GOTO 500
```

```

144 ETA = .0001
145 HOME : PRINT : PRINT
150 INPUT " Concentration      :
      ";X
160 IF X < (X(1) - ETA) OR X > =
      (X(22) + ETA) THEN PRINT : PRINT
      TAB( 7)"VALUE OUT OF RANGE"
      : FOR Q = 1 TO 2000: NEXT : GOTO
      145
170 INPUT " Temperature (K) :
      ";T
180 INPUT " Pressure (Pa) :
      ";P
200 FOR I = 1 TO N
210 IF (X(I) - ETA) < = X AND X
      < (X(I) + ETA) THEN K = 0:J
      = I:I = N: GOTO 230
220 IF X < (X(I + 1) - ETA) THEN
      K = 1:J = I:I = N: GOTO 230
230 NEXT I
250 IF K = 0 THEN GOSUB 1000: GOTO
      270
260 GOSUB 2000
270 GOSUB 3000
290 PR# 1
295 PRINT
300 PRINT TAB( 5)" ALPHA
      "=";A
302 PRINT TAB( 5)"HEAT CAPACITY
      "=";E
304 PRINT TAB( 5)" ENTROPY
      "=";C
306 PRINT TAB( 5)"VAP ENTHALPHY
      "=";D
310 PR# 0
315 FOR Q = 1 TO 2000: NEXT Q
320 GOTO 590
330 PRINT : PRINT
340 INPUT " Another value ? (ye
      s/no)";R$
350 IF R$ = "YES" THEN GOTO 145
360 IF R$ = "NO" THEN PRINT : PRINT
      : END
370 GOTO 320

```

500 B(1) = 175.14:C(1) = 148.051:  
D(1) = - 12.313  
501 B(2) = 173.30:C(2) = 149.268:  
D(2) = - 11.41  
502 B(3) = 170.16:C(3) = 150.574:  
D(3) = - 10.481  
503 B(4) = 165.43:C(4) = 151.95:D  
(4) = - 9.535  
504 B(5) = 159.07:C(5) = 153.381:  
D(5) = - 8.581  
505 B(6) = 155.66:C(6) = 154.1:D(  
6) = - 8.1  
506 B(7) = 151.84:C(7) = 154.812:  
D(7) = - 7.64  
507 B(8) = 148.33:C(8) = 155.5:D(  
8) = - 7.25  
508 B(9) = 144.51:C(9) = 156.117:  
D(9) = - 6.74  
509 B(10) = 140.66:C(10) = 156.8:  
D(10) = - 6.25  
510 B(11) = 137.95:C(11) = 157.29  
7:D(11) = - 5.895  
511 B(12) = 135.33:C(12) = 157.9:  
D(12) = - 5.5  
512 B(13) = 132.63:C(13) = 158.36  
4:D(13) = - 5.096  
513 B(14) = 130.66:C(14) = 158.8:  
D(14) = - 4.75  
514 B(15) = 128.57:C(15) = 159.33  
1:D(15) = - 4.343  
515 B(16) = 125.81:C(16) = 160.11  
7:D(16) = - 3.657  
516 B(17) = 124.14:C(17) = 160.67  
8:D(17) = - 3.058  
517 B(18) = 123.51:C(18) = 160.94  
6:D(18) = - 2.569  
518 B(19) = 123.64:C(19) = 161.01  
3:D(19) = - 2.155  
519 B(20) = 124.43:C(20) = 161.03  
8:D(20) = - 1.774  
520 B(21) = 125.69:C(21) = 160.98  
3:D(21) = - 1.443  
521 B(22) = 127.11:C(22) = 160.78  
7:D(22) = - 1.171

```

522 GOTO 144
590 R = 8.3143 * 10 ^ - 3
591 T0 = 298.15
592 A2 = 32.886 * 10 ^ - 3
593 B2 = 193.09 * 10 ^ - 6
594 C2 = - 10.9286 * 10 ^ - 8
595 K1 = A2 * T0 + (B2 * T0 * T0 /
      2) + (C2 * T0 * T0 * T0 / 3)

596 K2 = 289.074 * 10 ^ - 3
597 K3 = K2 - A2 - (B2 * T0) - (C
      2 * T0 * T0 / 2)
600 A1 = T0 * A * 10 ^ - 5 - B *
      10 ^ - 3 + A2
610 B1 = D + K1 - B * 10 ^ - 3 *
      T0 + (A * 10 ^ - 5 * T0 * T
      0 / 2)
620 C1 = K3 + B * 10 ^ - 3 - C *
      10 ^ - 3 - (A1 * LOG (T0))

630 D1 = (B2 - A * 10 ^ - 5) / 2

640 E1 = C2 / 6
650 H1 = A1 * LOG (T)
660 H2 = B1 / T
670 H4 = D1 * T
680 H5 = E1 * T * T
690 H6 = R * LOG (P / 101325)
700 H = (H1 + H2 + C1 + H4 + H5 -
      H6) * T
710 HOME : PRINT : PRINT
715 PR# 1
717 PRINT
720 PRINT " Concentration      : "
      ;X;" H2SO4 mole fraction"
730 PRINT " Temperature       : "
      ;T;" Kelvin"
740 PRINT " Pressure          : "
      ;P;" Pascals"
750 PRINT " Enthalpy of vaporiza
      tion :";H;" KJoules/mole"

```

```

762 PRINT
765 PR# 0
770 HOME
780 GOTO 330
1000 A = A(J)
1010 B = B(J):C = C(J):D = D(J)
1500 RETURN
2000 X1 = (X - X(J)) / (X(J + 1) -
X(J))
2010 A = A(J) + X1 * (A(J + 1) -
A(J))
2020 B = B(J) + X1 * (B(J + 1) -
B(J))
2030 C = C(J) + X1 * (C(J + 1) -
C(J))
2040 D = D(J) + X1 * (D(J + 1) -
D(J))
2500 RETURN
3000 X = INT (X * 10000 + .5) /
10000
3010 A = INT (A * 10000 + .5) /
10000
3020 B = INT (B * 10000 + .5) /
10000
3030 C = INT (C * 10000 + .5) /
10000
3040 D = INT (D * 10000 + .5) /
10000
3500 RETURN

```

Computer programme for the calculation of  
partial pressures

```
100 N = 22
110 DIM X(N),A(N)
115 DIM B(N),C(N),D(N)
120 X(1) = .444:A(1) = 6.25
121 X(3) = .465:A(3) = - 11.38
122 X(2) = .454:A(2) = - 2.05
123 X(4) = .476:A(4) = - 21.84
124 X(5) = .488:A(5) = - 32.68
125 X(6) = .494:A(6) = - 35.50
126 X(7) = .5:A(7) = - 36.86
127 X(8) = .506:A(8) = - 35.5
128 X(9) = .512:A(9) = - 33.26
129 X(10) = .520:A(10) = - 25.5
130 X(11) = .526:A(11) = - 17.03

131 X(12) = .533:A(12) = - 7.5
132 X(13) = .54:A(13) = - .62
133 X(14) = .547:A(14) = 4.75
134 X(15) = .555:A(15) = 9.2
135 X(16) = .571:A(16) = 14.52
136 X(17) = .588:A(17) = 17.70
137 X(18) = .606:A(18) = 20.04
138 X(19) = .625:A(19) = 21.5
139 X(20) = .645:A(20) = 22.51
140 X(21) = .666:A(21) = 23.09
141 X(22) = .690:A(22) = 23.43
142 GOTO 500
```

```

144 ETA = .0001
145 HOME : PRINT : PRINT
150 INPUT " Concentration      :
      ";X
160 IF X < (X(1) - ETA) OR X > =
      (X(22) + ETA) THEN PRINT : PRINT
      TAB( 7)"VALUE OUT OF RANGE"
      : FOR Q = 1 TO 2000: NEXT : GOTO
      145
170 INPUT " Temperature (K)  :
      ";T
200 FOR I = 1 TO N
210 IF (X(I) - ETA) < = X AND X
      < (X(I) + ETA) THEN K = 0:J
      = I:I = N: GOTO 230
220 IF X < (X(I + 1) - ETA) THEN
      K = 1:J = I:I = N: GOTO 230
230 NEXT I
250 IF K = 0 THEN GOSUB 1000: GOTO
      270
260 GOSUB 2000
270 GOSUB 3000
290 PR# 1
295 PRINT
300 PRINT TAB( 5)" ALPHA
      =" ;A
302 PRINT TAB( 5)"HEAT CAPACITY
      =" ;B
304 PRINT TAB( 5)" ENTROPY
      =" ;C
306 PRINT TAB( 5)"VAP ENTHALPY
      =" ;D
310 PR# 0
315 FOR Q = 1 TO 2000: NEXT Q
320 GOTO 590
330 PRINT : PRINT
340 INPUT " Another value ? (ye
      s/no)";R$
350 IF R$ = "YES" THEN GOTO 145

360 IF R$ = "NO" THEN PRINT : PRINT
      : END
370 HOME : PRINT : PRINT : GOTO
      340

```

500 B(1) = 175.14:C(1) = 148.051:  
D(1) = - 12.313  
501 B(2) = 173.30:C(2) = 149.268:  
D(2) = - 11.41  
502 B(3) = 170.16:C(3) = 150.574:  
D(3) = - 10.481  
503 B(4) = 165.43:C(4) = 151.95:D  
(4) = - 9.535  
504 B(5) = 159.07:C(5) = 153.381:  
D(5) = - 8.581  
505 B(6) = 155.66:C(6) = 154.1:D(  
6) = - 8.1  
506 B(7) = 151.84:C(7) = 154.812:  
D(7) = - 7.64  
507 B(8) = 148.33:C(8) = 155.5:D(  
8) = - 7.25  
508 B(9) = 144.51:C(9) = 156.117:  
D(9) = - 6.74  
509 B(10) = 140.66:C(10) = 156.8:  
D(10) = - 6.25  
510 B(11) = 137.95:C(11) = 157.29  
7:D(11) = - 5.895  
511 B(12) = 135.33:C(12) = 157.9:  
D(12) = - 5.5  
512 B(13) = 132.63:C(13) = 158.36  
4:D(13) = - 5.096  
513 B(14) = 130.66:C(14) = 158.8:  
D(14) = - 4.75  
514 B(15) = 128.57:C(15) = 159.33  
1:D(15) = - 4.343  
515 B(16) = 125.81:C(16) = 160.11  
7:D(16) = - 3.657  
516 B(17) = 124.14:C(17) = 160.67  
8:D(17) = - 3.058  
517 B(18) = 123.51:C(18) = 160.94  
6:D(18) = - 2.569  
518 B(19) = 123.64:C(19) = 161.01  
3:D(19) = - 2.155  
519 B(20) = 124.43:C(20) = 161.03  
8:D(20) = - 1.774  
520 B(21) = 125.69:C(21) = 160.98  
3:D(21) = - 1.443  
521 B(22) = 127.11:C(22) = 160.78  
7:D(22) = - 1.171  
522 GOTO 144



```

590 R = 8.3143 * 10 ^ - 3
591 T0 = 298.15
592 A2 = 32.856 * 10 ^ - 3
593 B2 = 193.09 * 10 ^ - 6
594 C2 = - 10.9286 * 10 ^ - 8
595 K1 = A2 * T0 + (B2 * T0 * T0 /
      2) + (C2 * T0 * T0 * T0 / 3)

596 K2 = 289.074 * 10 ^ - 3
597 K3 = K2 - A2 - (B2 * T0) - (C
      2 * T0 * T0 / 2)
600 A1 = T0 * A * 10 ^ - 5 - B *
      10 ^ - 3 + A2
610 B1 = D + K1 - B * 10 ^ - 3 *
      T0 + (A * 10 ^ - 5 * T0 * T
      0 / 2)
615 B3 = B1 - 79.54
620 C1 = K3 + B * 10 ^ - 3 - C *
      10 ^ - 3 - (A1 * LOG (T0))

630 D1 = (B2 - A * 10 ^ - 5) / 2

640 E1 = C2 / 6
650 H1 = A1 * LOG (T)
660 H2 = B3 / T
670 H4 = D1 * T
680 H5 = E1 * T * T
690 H6 = (H1 + H2 + C1 + H4 + H5)
      / R
700 P = EXP (H6) * 101325
710 HOME : PRINT : PRINT
715 PR# 1
717 PRINT
720 PRINT " Concentration      #"
      ;X;" H2SO4 mole fraction"
730 PRINT " Temperature      #"
      ;T;" Kelvin"
740 PRINT " Pressure          #"
      ;P;" Pascals"
762 PRINT

```

```

765  FR# 0
780  GOTO 330
1000 A = A(J)
1010 B = B(J):C = C(J):D = D(J)
1500  RETURN
2000 X1 = (X - X(J)) / (X(J + 1) -
      X(J))
2010 A = A(J) + X1 * (A(J + 1) -
      A(J))
2020 B = B(J) + X1 * (B(J + 1) -
      B(J))
2030 C = C(J) + X1 * (C(J + 1) -
      C(J))
2040 D = D(J) + X1 * (D(J + 1) -
      D(J))
2500  RETURN
3000 X = INT (X * 10000 + .5) /
      10000
3010 A = INT (A * 10000 + .5) /
      10000
3020 B = INT (B * 10000 + .5) /
      10000
3030 C = INT (C * 10000 + .5) /
      10000
3040 D = INT (D * 10000 + .5) /
      10000
3500  RETURN

```

### APPENDIX 3

HAASE & BORGMANN and HAASE & REHSE

$\Delta H_{H_2SO_4}$  values

HAASE & BORGMANN'S and HAASE & REHSE experimental results were analysed for  $\Delta H_{H_2SO_4}$  using the computer programme in Appendix 2. The results clearly shows a wide range of variation in the calculated value for the enthalpy of vaporisation of sulphuric acid. This could have happen due to dissociation of sulphuric acid as discussed in Chapter 5.

X MOLE fraction [H <sub>2</sub> SO <sub>4</sub> ]	T (C)	HASSE & REHSE P <sub>H<sub>2</sub>SO<sub>4</sub></sub> (Pa)	Δ H (kJ/mol)
0.128	57.8	9.2 E-6	65.83
0.128	66.7	8.93 E-6	69.01
0.128	81.3	5.2 E-5	68.91
0.128	81.9	1.14 E-4	66.78
0.128	87.4	1.46 E-4	67.85
0.128	87.5	2.26 E-4	66.57
0.128	87.6	1.09 E-4	68.79
0.128	87.9	1.86 E-4	67.29
0.128	90.2	2.00 E-4	67.82
0.128	100.2	6.66 E-4	67.34
0.128	106.1	1.05 E-3	67.76
0.128	116.5	3.6 E-3	67.03
0.128	72.7	1.7 E-5	69.19
0.128	73.5	4.2 E-5	66.87
0.165	65.3	1.86 E-5	72.21
0.165	68.8	4.8 E-5	70.70
0.165	73.9	5.2 E-5	72.15
0.165	79.1	6.66 E-5	73.13
0.165	84.2	3.06 E-4	70.26
0.165	99.5	4.93 E-4	73.59
0.165	111.4	2.13 E-3	72.61
0.165	119.4	3.6 E-3	73.29
0.165	125.0	8.0 E-3	72.29

X MOLE fraction [H <sub>2</sub> SO <sub>4</sub> ]	T (C)	HASSE & REHSE P <sub>H<sub>2</sub>SO<sub>4</sub></sub> (Pa)	Δ H (kJ/mol)
0.226	71.7	3.2 E-2	74.30
0.226	77.5	6.4 E-2	74.07
0.226	87.2	1.16 E-2	75.22
0.226	97.0	3.33 E-2	74.88
0.226	105.9	6.26 E-2	75.45
0.226	119.7	0.018	75.83
0.226	133.4	0.054	75.84
0.226	141.5	0.08	76.65
0.282	98.5	0.014	76.69
0.282	105.9	0.024	77.03
0.282	115.9	0.041	77.88
0.282	122.2	0.068	77.85
0.282	132.1	0.112	78.64
0.282	139.6	0.18	78.84
0.282	150.3	0.36	78.94
0.282	158.7	0.52	79.56
0.314	117.7	0.077	79.1
0.314	124.4	0.14	78.80
0.314	128.4	0.164	79.22
0.314	139.0	0.32	79.40
0.314	143.5	0.493	78.92
0.314	164.5	1.33	79.90
0.314	171.5	2.00	79.85
0.400	122.0	0.4	80.61
0.400	148.1	2.66	79.60
0.400	158.3	4.93	79.3
0.400	179.2	16.00	78.82
0.400	191.4	40.00	77.36
0.400	196.7	45.33	77.72

X MOLE fraction [H <sub>2</sub> SO <sub>4</sub> ]	T (C)	HAASE & REHSE		$\Delta H$ (kJ/mol)
			PH <sub>2</sub> SO <sub>4</sub> (Pa)	
0.511	125.8		2.53	80.65
0.511	160.0		22.66	79.88
0.511	176.3		48.00	80.16
0.511	181.9		68.00	79.87
0.511	198.9		146.66	79.93
0.511	208.6		253.33	79.40
0.511	228.6		573.33	79.44
0.641	154.6		32.4	80.36
0.641	163.4		45.6	80.67
0.641	178.5		102.13	80.28
0.641	186.6		168.00	79.66
0.641	208.4		364.00	80.00
0.641	217.9		700.00	78.75
0.641	239.6		1426.66	78.78
0.641	246.8		2200.00	77.87
0.641	267.4		4080.00	77.73
0.813	224.3		1.6	78.00
0.813	241.1		3.05	77.57
0.813	260.7		5.96	77.01
0.813	275.9		10.32	76.25
0.813	287.5		14.93	75.78
0.813	296.3		21.06	75.06
0.813	304.4		26.80	74.71
0.813	315.1		37.33	74.11
0.885	195.6		0.6	78.70
0.885	273.2		11.90	75.93
0.885	296.5		30.40	73.97
0.885	322.0		56.80	73.30
0.885	239.8		3.65	77.26

X MOLE fraction [H <sub>2</sub> SO <sub>4</sub> ]	T (C)	HAASE & BORGMANN		$\Delta H$ (kJ/mol)
		P <sub>H<sub>2</sub>SO<sub>4</sub></sub>	(Pa)	
0.410	140.5	1.25		81.25
0.410	150.0	2.66		80.52
0.410	160.1	5.33		79.99
0.410	166.3	8.13		79.60
0.410	179.8	20.00		78.64
0.410	192.7	40.00		78.12
0.410	140.6	1.19		81.46
0.410	149.0	2.32		80.82
0.410	160.0	5.47		79.88
0.410	165.9	8.13		79.52
0.410	180.3	17.87		79.15
0.410	193.2	41.33		78.08
0.410	141.3	1.28		81.34
0.410	150.0	2.4		80.89
0.410	159.5	5.33		79.87
0.410	165.5	7.6		79.70
0.410	180.5	19.06		78.93
0.410	190.3	38.66		77.87
0.343	110.8	0.065		80.16
0.343	120.0	0.146		79.74
0.343	129.8	0.307		79.54
0.343	140.0	0.613		79.43
0.343	150.0	1.24		79.09
0.343	160.0	2.40		78.76
0.343	170.0	5.06		77.98
0.343	180.0	9.86		77.34
0.343	110.4	0.065		80.06
0.343	119.5	0.157		79.39
0.343	130.4	0.346		79.26
0.343	139.8	0.666		79.10
0.343	149.8	1.31		78.87
0.343	160.6	2.66		78.50
0.343	171.5	5.33		78.07
0.343	120.1	0.155		79.58
0.343	129.5	0.320		79.33
0.343	139.0	0.613		79.21
0.343	149.0	1.25		78.85
0.343	159.0	2.55		78.35
0.343	171.6	5.20		78.18

X MOLE fraction [H <sub>2</sub> SO <sub>4</sub> ]	T (C)	HAASE & RORGMANN P <sub>H<sub>2</sub>SO<sub>4</sub></sub> (Pa)	Δ H (kJ/mol)
0.318	119.7	0.091	79.42
0.318	130.2	0.227	78.87
0.318	140.4	0.453	78.82
0.318	150.0	0.826	78.83
0.318	159.8	1.46	78.86
0.318	169.8	3.07	78.20
0.318	120.5	0.109	79.00
0.318	130.0	0.213	79.02
0.318	139.8	0.413	79.01
0.318	150.0	0.733	79.25
0.318	159.7	1.33	79.18
0.318	170.0	3.07	78.24
0.318	121.0	0.111	79.08
0.318	129.5	0.20	79.12
0.318	140.4	0.427	79.03
0.318	151.0	0.813	79.11
0.318	160.5	1.6	78.69
0.318	169.1	3.07	78.07
0.283	100.1	0.015	77.13
0.283	110.0	0.029	77.56
0.283	120.1	0.055	78.13
0.283	130.0	0.121	77.95
0.283	140.1	0.200	78.68
0.283	150.0	0.373	78.83
0.283	159.8	0.573	79.54
0.283	100.2	0.013	77.42
0.283	110.9	0.031	77.65
0.283	120.0	0.059	77.88
0.283	131.4	0.131	78.04
0.283	138.2	0.192	78.37
0.283	151.8	0.387	79.12
0.283	156.9	0.547	79.05
0.283	100.9	0.015	77.26
0.283	110.9	0.031	77.65
0.283	119.5	0.056	77.90
0.283	130.5	0.128	77.89
0.283	139.4	0.187	78.75
0.283	149.1	0.347	78.88
0.283	159.9	0.613	79.32



X MOLE fraction [H <sub>2</sub> SO <sub>4</sub> ]	T (C)	HAASE & BORGMANN P <sub>H<sub>2</sub>SO<sub>4</sub></sub> (Pa)	Δ H (kJ/mol)
0.256	90.0	0.006	74.13
0.256	100.0	0.013	74.76
0.256	110.3	0.028	75.19
0.256	120.0	0.053	75.72
0.256	129.8	0.096	76.19
0.256	140.0	0.147	77.29
0.256	150.0	0.240	78.02
0.256	100.1	0.012	74.98
0.256	110.9	0.030	75.06
0.256	121.0	0.052	75.98
0.256	130.0	0.085	76.63
0.256	139.4	0.208	75.94
0.256	150.0	0.231	78.09