A THERMODYNAMIC STUDY OF HIGH TEMPERATURE EQUILIBRIA INVOLVING ZINC CHLORIDE

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Abstract

Molten zinc chloride has been used as a solvent and catalyst for the hydrocracking of heavy oils and coal slurries. Although there has been some systematic study of the mechanism of these catalytic reactions, little attention has been directed to the fate of the inorganic species which accumulate in the melt. These species derive from heteroatoms in the feedstock, and comprise mainly of zinc sulphide, zinc oxide, zinc-ammine chlorides and other minor chloride complexes. Their steady accumulation poisons the catalyst and renders it cost-inefficient.

This research aims (i) to appraise the available thermodynamic data and (ii) to determine such thermodynamic parameters as are necessary to define equilibria involving zinc-containing species in a zinc chloride melt.

The experimental technique used in this work is the Modified Entrainment Method (MEM). The principal modification of our method from conventional entrainment (or transpiration) is to isolate the sample from the flowing gas stream by a capillary of well-defined geometry so permitting equilibrium partial pressures to obtain above the sample. In this manner equilibrium thermodynamic results may be derived that are independent of the flow rate. A new

design of silica capsule involving a re-entrant capillary has been developed for the MEM which replaces the earlier flared capillaries and eliminates the correction for their variable geometry.

The following systems have been studied:

1) the vaporisation of $ZnCl_2$ involving monomer and dimer species (360 to 710°C),
2) the reductive transport of ZnS in H_2 (740 to 1180°C) (including the phase transition $ZnS_{\beta\rightarrow\alpha}$ (1020°C)).
3) the transport of ZnS by HCl (750 to 990°C),
4) the thermal dissociation of $ZnCl_2(NH_3)_2$ (170 to 400°C), and
5) the diffusion of Zn(g) in H_2, He, N_2 and Ar (420 to 870°C) and of Hg(g) in the same gases (150 to 320°C).

Dedication

Revinder Pang, Liu Chow Hop and Chai Wan Pang,
my Wife, Mother and Father,
in gratitude for that rare thing -
an act of total understanding kindness.

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It is with great pleasure that I acknowledge the help and guidance of Dr. P.J. Gardner (University Supervisor) for constructive criticism, penetrating remarks and supportive friendship during both the course of this work and the preparation of my thesis.

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Finally, I thank my wife, Ravi, and my family for suffering, without complaint, the brutishness to which authors sink in order to create something they hope is worthwhile.

I hear, and I forget.
I see, and I remember.
I do, and understand.
Ten Thousand words not worth one seeing.

Chinese Proverbs.

我聽到和忘記
我看到和記得
我做和明白
萬字不能夠代替
看到的。

中國諺語

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Joint Authors P.J. Gardner and P. Pang.

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3. The Thermodynamics of Zinc Sulphide Transport in Hydrogen Chloride by Modified Entrainment.
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Chapter 1

Introduction

1.1 Introduction

The use of metal halides as catalysts in coal hydrogenation before 1940 has been well documented by Storch[1]. This early work involved small quantities (often less than 5%) impregnated on the coal, and was developed to the pilot plant stage by several international oil companies. The use of molten zinc chloride for coal liquefaction was originally exploited by Gorin and co-workers at Consolidation Coal Company (now Conoco Coal Development Company) in 1960. Zinc chloride was found to be much more active and selective in hydrocracking coal than conventional sulphur-resistant catalysts, providing that the molten salt was used in unconventionally large amounts. Of the salts tested, zinc chloride was chosen because of its superior product distribution, remarkable resistance to hydrolysis and low cost. Extended research with zinc chloride lead to a process for converting coal to liquid fuels that has been demonstrated in a continuous bench-scale hydrocracker and in a 45 kg h^{-1} catalyst regeneration unit[2,3].

The process consists of two main steps (1) hydrocracking and (2) catalyst regeneration.

Hydrocracking is conducted in a pool of molten zinc chloride typically at 420°C, a hydrogen overpressure of 17 MPa and with a zinc chloride to coal feed ratio of 1.0. The spent melt is contaminated with hydrocarbonaeous residue, coal ash, nitrogen (as $ZnCl_2.NH_3$), sulphur (as ZnS) and oxygen (as ZnO), impurities arising from the heteroatoms in the feedstock. The regeneration is effected in a fluidized-bed combustor where the zinc chloride is vaporised and impurities are converted to N_2, H_2O and SO_2 at 900°C at a pressure of 0.5 MPa.

Recently hydrocracking of heavy grades of crude oils using zinc chloride as a weak Lewis acid catalyst have been commercially explored to selectively produce high yields of gasoline but only limited information on process conditions is available from the general and patent literature.

Although there has been some systematic study of the mechanism of the hydrocracking reaction[4], little attention has been directed to the fate of the inorganic species which accumulate in the melt. The chemical constitution of these heteroatoms in the feedstock, heavy oils or coal, is irrelevant because reaction conditions (overpressure of hydrogen at 420°C) in the melt are sufficiently forcing to convert N, O, and S into NH_3, H_2O and H_2S which interact with zinc chloride catalyst to give an ammonia chloride complex, an oxide and a sulphide

$$ZnCl_2 + NH_3 = ZnCl_2.NH_3$$

$$ZnCl_2 + H_2O = ZnO + 2HCl$$

$$ZnCl_2 + H_2S = ZnS + 2HCl$$

Their steady accumulation (and including possibly $VOCl_2$ and $NiCl_2$) act so as to poison the catalyst rendering it cost-inefficient. A recent regeneration patent[3] for the removal of these inorganic species exists. However there are only limited reliable thermodynamic data on the above reactions and still less information on their kinetics. Neverthless, it is a fair assumption that at the process operating temperature the yields of these inorganic species are thermodynamically controlled.

1.2 Objective

This research work aims to appraise the available data and to determine such thermodynamic parameters as are necessary to define equilibria involving zinc-containing species in a contaminated zinc chloride melt. Three equilibria of pivotal importance in this system are reactions (1), (2) and (3).

$$ZnCl_2(liq) + H_2S(g) = ZnS(soln) + 2HCl(g) \quad (1)$$

$$ZnCl_2(liq) + H_2O(g) \quad = \quad ZnO(soln) + 2HCl(g) \quad (2)$$

$$ZnCl_2(liq) + NH_3(g) \quad = \quad ZnCl_2.NH_3(soln) \quad (3)$$

where soln refers to a mixture with the $ZnCl_2$ melt only. Thermodynamic data for equilibria (1) to (3) above may be obtained directly or indirectly. This thesis investigates directly these equilibria over a temperature range of 150 to 1200°C using the Modified Entrainment Method.

1.3 Method of Obtaining Thermodynamic Data

The thermodynamics of heterogeneous equilibria provides the corner-stone for many branches of physical and chemical science, for example, material preparation, corrosion and combustion. Vapour pressures and dissociation pressures have been measured by manometry, effusion, torsion-effusion, mass spectrometry, calorimetry and entrainment methods. A similar variety of techniques is available for determining equilibrium constants for chemical reactions[5]. For vapour-solid and vapour-liquid reactions, entrainment (also known as transipartion) has long been a popular method. Before outlining the modified entrainment method, a brief summary of conventional entrainment is presented.

A carrier gas (sometimes doped with a reactive component) is passed over the solid or liquid sample maintained at a fixed temperature. The amount of product formed in a given time is found and the total volume of carrier gas used is noted. The product is determined from the loss of weight of the solid or liquid, or by condensing or dissolving the sublimate out of the gas stream and determining them by standard analytical techniques. This method is both simple and flexible. However, it suffers from the disadvantage that the effect of the flowing carrier or reactive gas at a finite rate must be accounted for or eliminated. If the gas-flow is very fast, the vapour is not fully equilibrated with the condensed phase, whereas if the flow is very slow, products may travel away from the zone in which equilibrium is being established by diffusion. Furthermore, unmixing of the gas by thermal diffusion becomes a serious source of error, particularly if the gas mixture contains hydrogen[6]. Traditionally, extrapolation to zero flow rate has been used, but this can result in error for the reasons given above. By constricting the flow channel either side of the equilibrium zone containing the condensed phase the effect of diffusion at low flow rates can be reduced. If the apparent partial pressure of the product is plotted as a function of flow rate, there may be a range of flow rates in which the apparent partial pressure does not alter greatly, and this "plateau" value is often taken as representing the true partial pressure[7]. In a well-designed apparatus this assumption may be justifiable, but because equilibrium is established only at the surface of the condensed phase, there must always be some diffusion of reactants towards the surface and of products away from the surface. This region in which diffusion operates is ill-defined. Diffusion can be made less limiting by causing turbulent mixing of the gas in the reaction zone, or by flowing the gas stream fast to reduce the boundary layer over the solid or liquid. Inevitably there may be some composition change in the gas in a direction normal to the surface of the condensed phase, and this is an eventual limitation of the method. When a "plateau" in the plot of apparent partial pressure against flow rate is not found, the true partial pressure is in doubt.

The Modified Entrainment Method (MEM) comes to terms with the unavoidable diffusion effect by confining its region of action to a long narrow channel of known geometry (typically 20 mm long, 1 mm I.D.). Its operation is independent of flow rate established in separate experiments which ensure that the heterogenous equilibrium is closely approached over a wide range of temperatures. One end of the channel is connected to a bulb or reservoir containing the condensed phase under study, and the other end is directed into the stream of reactive gas (figure 1.1).

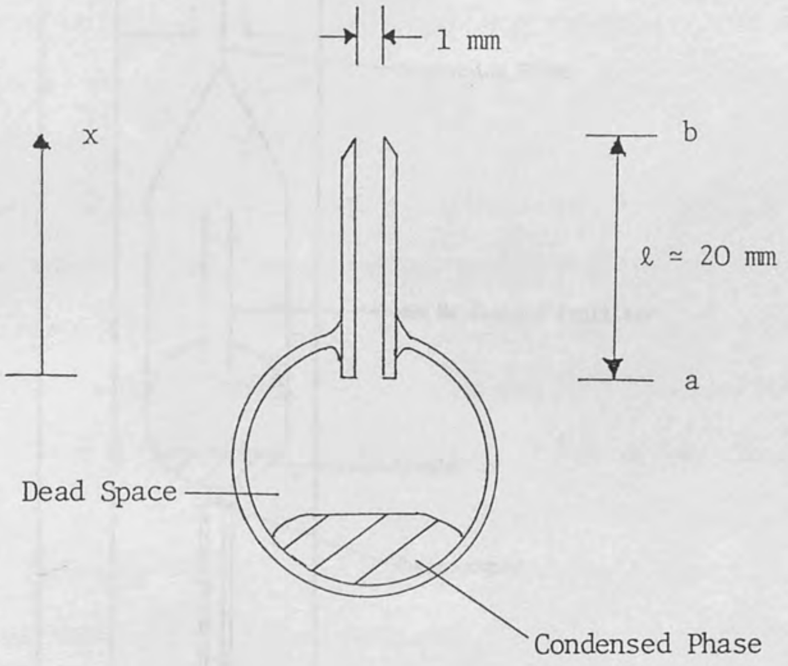

Figure 1.1 Re-entrant Design MEM Reaction Bottle

The reservoir and channel are suspended from a recording microbalance, so that the loss of weight can be measured continuously. By measuring this rate of weight loss, the partial pressures inside the bulb may be described accurately via a simple flux theory. This approach is not new, having been used by Stefan[8] in 1890 to measure the diffusion coefficient of ether in air. When the vapour leaves the open end of the channel, it is rapidly diluted and swept away in a fast stream of carrier gas.

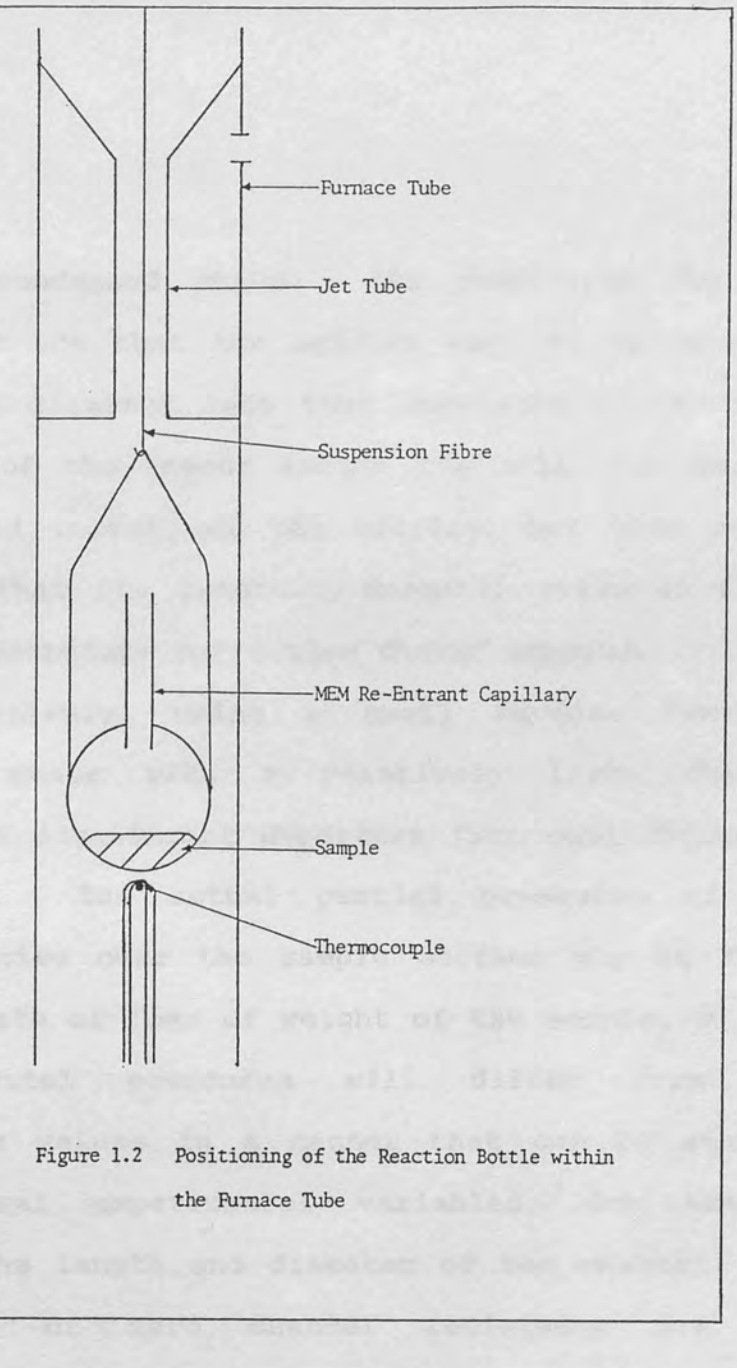

Figure 1.2 Positioning of the Reaction Bottle within the Furnace Tube

By using a narrow channel and increasing the surface area of the condensed phase in the MEM capsule, the chemical reaction or evaporation process at the surface can be made to limit the rate at which weight is lost. The technique has some similarity with Knudsen's method for measuring vapour pressures which relies on the measurement of the rate of effusion of a vapour through a small orifice in a gas-tight container where the vapour is at equilibrium with the condensed phase. The conditions for the measurement are that the orifice must be knife-edged and have a diameter less than one-tenth of the mean free path of the vapour inside the cell. A channel may be used instead of the orifice, but then it is important that its length-to-diameter ratio is known and the appropriate correction factor applied.

Alternatively, using a small surface area of condensed phase with a relatively large channel diameter, a significant departure from equilibrium is maintained. The actual partial pressures of the vapour species over the sample surface may be found from the rate of loss of weight of the sample, $\mathring{\omega}$, and those partial pressures will differ from the equilibrium values in a manner that can be studied with several experimental variables, for example changing the length and diameter of the channel. In the limit of zero channel resistance i.e. an infinitely wide short channel, the system reduces to Langmuir evaporation. Notice that while both Langmuir evaporation and Knudsen effusion[10] are performed at low pressure, modified entrainment is performed at approximately atmospheric pressure.

Another attractive feature of this method for studying chemical transport reactions is that, as it is a dynamic system, the transport rate $\mathring{\omega}$ cannot be affected by an accumulation of gaseous impurities or of a stoichiometric excess of one component of the sample. In common with other dynamic methods, the composition of the vapour inside the reaction bottle is such as to produce the maximum attainable rate of transport for the given composition of reactive gas flowing through the hot zone. By contrast in a static or sealed system the rate of transport can be reduced by orders of magnitude by the almost inevitable accumulation of unwanted vapour constituents[2].

1.4 Theoretical description of the Modified Entrainment Method for a single substance

The theory of the modified entrainment method has been fully documented and verified[11,12,13]. Here only a short summary will be given for a single substance although in subsequent Chapters and Appendix 2 of this thesis, examples of more complex reactions (dissociative sublimation and heterogenous equilibria) are fully discussed.

A one-dimensional model, see figures 1.1 and 1.2, may be used to describe gas transport in the channel through which vapour in the bulb of the sample bottle communicates with the external gas stream. For the evaporation of a liquid, or sublimation of a solid

$$M(\ell) = M(g) \qquad (1.4.1)$$

$$M(s) = M(g) \qquad (1.4.2)$$

there is a net increase in molar volume in the system. The vapour is not transported away from the surface by diffusion alone, since the increase in volume accompanying vaporisation (the driving force) gives rise to a Stefan[14] flow or "wind". Stefan verified experimentally, that the volume of vapour passing through unit cross-section of pipe (in this example a capillary) in unit time was given by

$$V = \frac{D}{P-p} \cdot \frac{dp}{dx} \qquad (1.4.3)$$

where P is the total pressure, p the partial pressure of the vapour, and *D* is the binary diffusion coefficient between evaporating vapour and inert carrier gas. This equation is obtained from Fick's first law.

The flux, J/mol $m^{-2}s^{-1}$, which measures the rate of flow of matter being transported from one region (inside the capsule) of a system to another (outside the capsule), arises from both convective flow (or Stefan "wind") and from diffusion.

$$J_i = n_i U - D \frac{dn_i}{dx} \qquad (1.4.4)$$

where U is the Stefan velocity, and n_i/mol m^{-3} is the molar density. At the base of the channel, see figure

1.1, where x = a, the vapour phase is assumed to contain the equilibrium vapour pressure of the condensed phase. Experimentally, this assumption is usually verified by noting the constancy of the flux using a range of different channel sizes. At the top of the channel where x = b, the vapour from the capillary is rapidly flushed and diluted by the bulk flow of the inert carrier gas, and consequently the vapour concentration here is negligible. The effect of rate of weight loss against varying flow rate has been studied for diffusion, sublimation and heterogenous systems[11,14,15], and found to be essentially independent of the entire range of flow 1 to 350 $cm^3\ min^{-1}$ used. Typically in this work flow rates in the range 70 to 100 $cm^3\ min^{-1}$ (s.t.p.) were used. Notice, the flow rate of the inert carrier gas must be sufficiently large to sweep away local concentration of vapour of the mouth of the channel and that its rate does not enter into subsequent flux equations that define the reaction of interest.

Flux equations for the reactants, products and carrier gas (for example, H_2) in the channel may be written in the following form

$$J_i = n_iU - D_{(i,H_2)} \frac{dn_i}{dx} \qquad (1.4.5)$$

where J_i is the flux of the species i, n_i is the concentration of species i, U is the mole-average Stefan velocity and $\mathcal{D}_{(i,H_2)}$ the binary diffusion coefficient of the species i in hydrogen. For dilute gases, ideal gas behaviour is assumed and the molar densities in equation (1.4.5) may be replaced by partial pressures from

$$n_i = \frac{n}{v} = \frac{p_i}{RT}$$

Using Poiseuille's formula for viscous flow in a capillary it can be shown that the total pressure varies negligibly with x unless the channel is very narrow[6].

Equation (1.4.5) may then be rewritten

$$J_i = \frac{Up_i}{RT} - \frac{\mathcal{D}_{(i,H_2)}}{RT}\frac{dp_i}{dx} \qquad (1.4.6)$$

For hydrogen, the inert carrier gas, there is no net flow so $J_{H_2} = 0$. On summation of the flux equations the diffusion terms cancels, if there is no pressure gradient in the channel, and

$$\textstyle\sum_i J_i = J = \frac{UP}{RT} \qquad (1.4.7)$$

where, $P = \sum_i p_i$, is the total pressure in the system.

Now substituting (1.4.7) in (1.4.6), the Stefan term U is eliminated

$$J_i = \frac{JRT}{P}\frac{p_i}{RT} - \frac{D_{(i,H_2)}}{RT}\frac{dp_i}{dx}$$

rearranging we obtain

$$\frac{RT}{D_{(i,H_2)}} J_i + \frac{dp_i}{dx} = \frac{Jp_i}{P}\frac{RT}{D_{(i,H_2)}}$$

and

$$\frac{dp_i}{dx} = \frac{RT}{D_{(i,H_2)}}\left[\frac{Jp_i}{P} - J_i\right] \qquad (1.4.8)$$

now separating the variables

$$\frac{dp_i}{(Jp_i/P) - J_i} = \frac{RT}{D_{(i,H_2)}}\,dx$$

Integrating from, x = a to x = b we obtain

$$\int_{P(a)}^{P(b)} \frac{dp_i}{(Jp_i/P) - J_i} = \int_a^b \frac{RT}{D_{(i,H_2)}}\,dx$$

$$\frac{P}{J}\ln\left[\frac{(Jp_i^{(b)}/P) - J_i}{(Jp_i^{(a)}/P) - J_i}\right] = \frac{RT\ell}{D_{(i,H_2)}}$$

so
$$\ln\left[\frac{(Jp_i^{(b)}/P)-J_i}{(Jp_i^{(a)}/P)-j_i}\right] = \frac{JRT\ell}{D_{(i,H_2)}P}$$

In order to simplify matters let us introduce ξ_i, the transport function of species i.

$$\xi_i = \frac{JRT\ell}{PD_{(i,H_2)}} = \frac{\mathring{\omega}RT\ell}{D_{(i,H_2)}AMP}$$

where, $J = \mathring{\omega}/AM$

$\mathring{\omega}/\mathrm{kg\ s^{-1}}$ = the rate of weight loss from the sample.

$R/\mathrm{J\ K^{-1}mol^{-1}}$ = the gas constant.

T/K = temperature.

$(b-a) = \ell/\mathrm{m}$ = the length of the MEM capsule channel.

$D_{(i,H_2)}/\mathrm{m^2s^{-1}}$ = the binary diffusion coefficient of species i in hydrogen.

$A/\mathrm{m^2}$ = the cross-sectional area of the MEM capsule channel.

$M/\mathrm{kg\ mol^{-1}}$ = the molecular mass of the condensed phase.

P/Pa = the total pressure.

Thus rearranging,

$$\frac{p_i^{(a)}}{P} = \frac{J_i}{J} - \left[\frac{J_i}{J} - \frac{p_i^{(b)}}{P}\right]e^{-\xi_i} \qquad (1.4.9)$$

Considering the evaporation of a single species (e.g. zinc in H_2) for a minority species (the vaporised atoms) it can be assumed that at the mouth of the capillary channel

$$\frac{p_i^{(b)}}{P} = 0$$

as previously mentioned, the species i is quantitatively swept away from the open end of the channel. Substituting this equation into equation (1.4.9) gives directly,

$$p_i^{(a)} = P(1 - e^{-\xi_i}) \qquad (1.4.10)$$

$P_i^{(a)}$ represents the saturated vapour pressure of the sample since in this case $J = J_i = 1$.

The only experiment parameters unknown are the partial pressure $p_i^{(a)}$ and the binary diffusion coefficient $D_{(i,H_2)}$ - consequently if one is known, the other may be determined. For this example of single substance evaporation, the vapour pressure is usually known and hence the method is used to obtain diffusion coefficients as a function of temperature.

1.5 Transport function ξ_i

In the modified entrainment method, the partial pressure (p_i) of the minority component in a two component system has been shown to be

$$p_i = P(1 - e^{-\xi_i}) \qquad (1.5.1)$$

where $\xi_i = \mathring{\omega} RT\ell/\mathcal{D}AMP$

in section 1.4. Such a system would be the evaporation of zinc in an argon or hydrogen carrier gas. The term, $(1 - e^{-\xi_i})$, may be approximated to ξ_i to an accuracy of 5% if the transport function, $\xi_i < 0.1$. In some cases it is necessary to retain a quadratic term in the exponential expansion when the same accuracy is obtainable for $\xi_i < 0.5$. Mass transport in the capillary is via diffusive and convective flow. Cussler[16] has shown that the first of the exponential approximations above is equivalent to the dilute gas approximation where mass transport is assumed to be exclusively diffusive. In systems where more than one component e.g. monomer and dimer, contribute to the transport this exponential approximation is nearly always invoked[11] because of algebraic tractability.

1.6 Subsequent Chapters

This introductory chapter covers only background material relevant to zinc chloride - catalysed hydrocracking and the modified entrainment method. The following chapters are self-contained and each contains a short introductory section in which the relevant literature is critically evaluated. This is a departure from the usual practice of collecting all introductory material into the first chapter. The Appendeces contain raw data including rate of weight loss as a function of temperature and pressure for each equilibrium studied. Other ancillary experimental details also included in the Appendeces are calibration of thermocouples, temperature profiles of furnaces, MEM algebraic transport equations of chemical equilibria and computer programs used in the MEM studies.

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Chapter 2

Experimental

* Words in italics refer to table 2.1 where details of manufacturer's specifications, model serial numbers, and retail addresses are collected. *

2.1 The Modified Entrainment Method (MEM) Rig

The MEM is a modification of the capillary leak method widely used for the determination of diffusion coefficients of gaseous species[1]. Modified entrainment was first validated by comparing the measured vapour pressure of water and lead with literature data[2]. Subsequent studies using the MEM have included the determination of binary gaseous diffusion coefficients[3], congruent sublimation[4], retarded sublimation[5], heterogeneous reaction kinetics[6] and other equilibria[7,8,9]. In this procedure a small silica capsule containing a condensed phase was suspended from one arm of a recording microbalance into the hot zone of a vertically mounted tube furance (figure 2.1). The capsule orifice is in the form of a vertical capillary (ca. 20mm long x 1mm internal diameter), which acts as a diffusive resistance isolating the condensed phase from the irreproducible effects of the flowing transport gas.

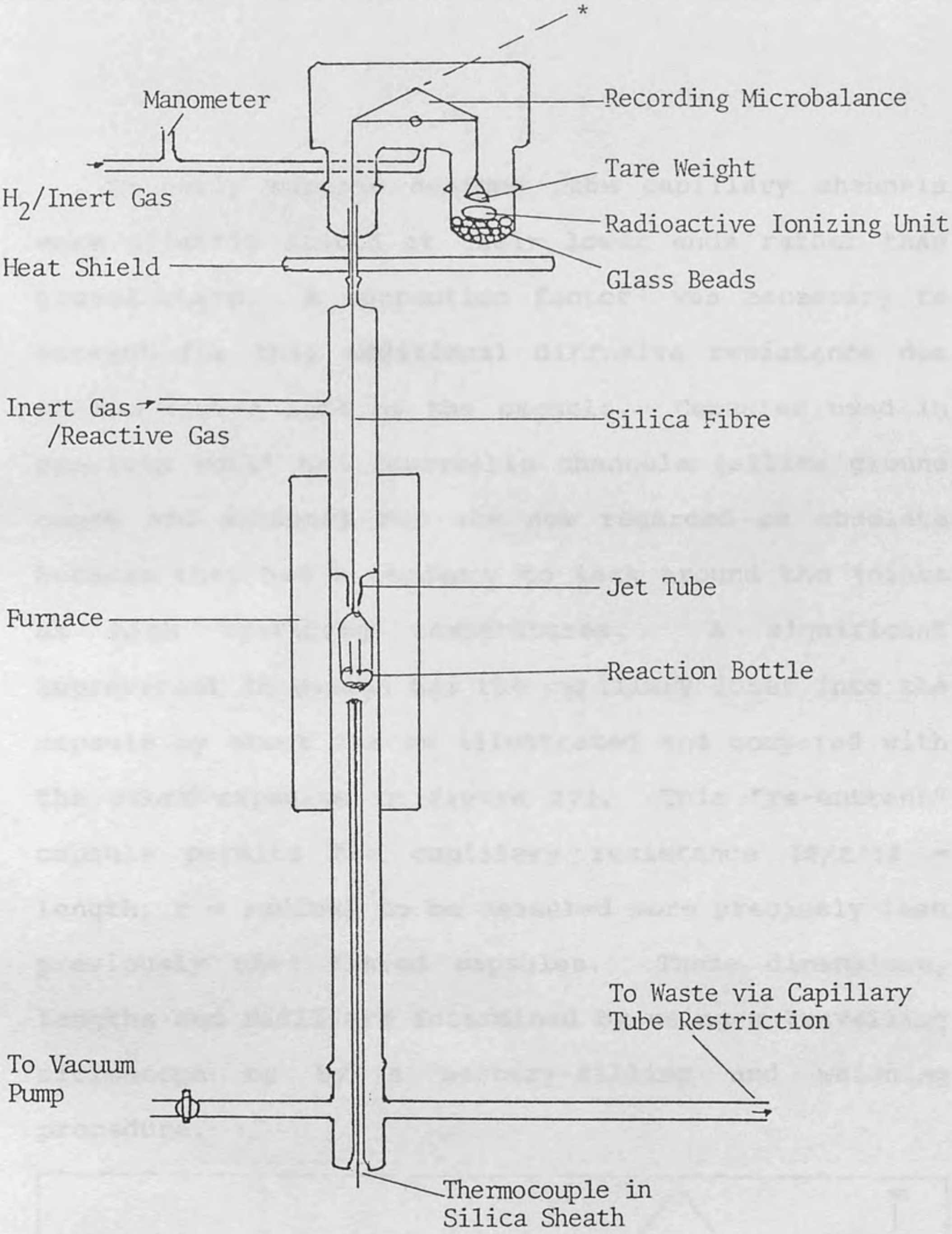


Figure 2.1 Modified Entrainment Rig

* Small fan behind to cool electrobalance from furnace

In early capusle designs, the capillary channels were slightly flared at their lower ends rather than ground sharp. A correction factor[7] was necessary to correct for this additional diffusive resistance due to the flared neck of the capsule. Capsules used in previous work[6] had removeable channels (silica ground cones and sockets) but are now regarded as obsolete because they had a tendency to leak around the joints at high operating temperatures. A significant improvement in design has the capillary inset into the capsule by about 2mm as illustrated and compared with the other capsules in figure 2.2. This "re-entrant" capsule permits the capillary resistance (ℓ/r^2: ℓ = length, r = radius) to be measured more precisely than previously used flared capsules. These dimensions, lengths and radii are determined by using a travelling microscope or by a mercury-filling and weighing procedure.

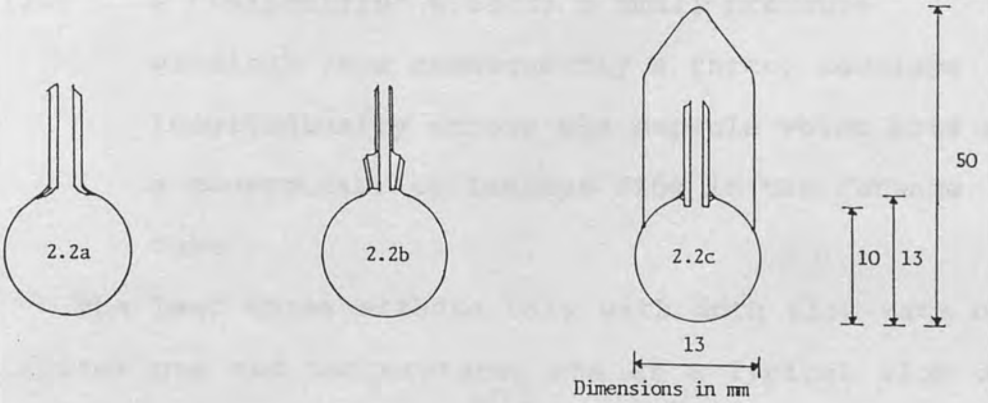


Figure 2.2 Design of MEM Capillary Channels
a) integral, b) demountable and c) re-entrant

The central component of the MEM apparatus was the *recording microbalance* from which was suspended the sample capsule, via a silica fibre with a maximum diameter of 400 micros. Thicker fibres were avoided because their stiffness often resulted in rubbing against the constrictor in the furnace tube (see figure 2.1); this was usually detected by a characteristic signal on the recorder output of mass versus time. The mass of the capsule in the MEM rig is different from a static determination in vacuo for several reasons

(i) an effect of buoyancy, the magnitude of which depends on the carrier gas and its temperature,

(ii) a momentum transfer effect; the downward flow of the carrier induces a net force on the upper surface of the capsule which enhances its mass,

(iii) a viscous drag effect caused by the gas stress passing over the capsule and

(iv) a "Poiseuille" effect; a small pressure gradient (and consequently a force) develops longitudinally across the capsule which acts as a constructor to laminor flow in the furnace tube.

The last three effects vary with both flow rate of carrier gas and temperature, and at a typical flow of 80 cm^3min^{-1} (stp), sum to ≃ 0.4 mg. This thermal gas flow[10] is particularly troublesome as the operating temperature increases. Random fluctuations were more pronounced in nitrogen and argon flow than in hydrogen or helium.

Electrostatic forces acting between the silica fibre and the furnace tube can become so strong as to displace the sample bottle laterally where it will rub causing excessive noise on the mass versus time recorder trace. Several techniques were employed during operation of the rig to prevent and overcome this problem

(i) the rig operator does not wear a synthetic fibre, for example nylon laboratory overall,

(ii) use of an *anti-static work station* kit (consisting of wrist straps, tray, bench and floor mats connected to a ground source),

(iii) a *radioactive ionizing unit* on the counter weight balance side to eliminate charge build-up on the tare pan,

(iv) making sure the silica fibre has attached to a heavily waded bottle (approx. 1g) and

(v) making the support fibre as thin as possible to hang straight down without touching the constrictor tube.

The microbalance has a maximum sample capacity of 100g and an electrical lifting capacity of 10g, with a maximum sensitivity of 5×10^{-10} kg. Microgravimetric measurements were usually operated at a sensitivity of

1×10^{-8} kg, with the meter and recorder range (MMR) set to 1 mg which determined the amount of weight that has displayed, full scale, on the meter, recorder or other readout device (digital voltmeter) used. The experimental parameter, the rate of mass loss varied between 1×10^{-8} to 1×10^{-12} kg s^{-1}.

The capsule was held under isothermal conditions in a temperature range of 350 to 1170°C by a *demountable tube furnace* consisting of two 920 W hemicylindrical elements each 450mm long and with a 45mm internal diameter. The temperature was controlled by a *linear temperature variable rate programmer* coupled to a controlling thermocouple located between the furnace wall and the furnace tube. Sample temperatures were monitored by a second thermocouple, sheathed in a thin-walled silica tube positioned axially 2mm below the capsule (see figure 2.1). Both sensing and monitoring thermocouples are type R, Pt/Pt-13%Rh fabricated from wire supplied by Johnson Matthey Metals Ltd. The monitoring thermocouple was calibrated against a secondary standard type R thermocouple which itself was calibrated at a commercial calibration laboratory (Harwell Instrument Test Laboratories, temperature points taken at 601, 801, 1000°C to a precision of ± 2 K). The measuring thermocouple was connected via a *cold junction reference compensator* to a *digital* *voltmeter* displaying the thermal emf. This thermocouple voltage was converted into temperature using polynominal equations based on IPTS-68 (International Practical Temperature Scale of 1968)[11]. A detailed examination of the temperature profiles along the long axis of the tube furnace with set temperatures between 400 to 1200°C was completed. The shape of the profiles was improved by insulating the bottom of the furnace with *ceramic wool fibre*. This generated a 40mm plateau with a temperature variation of ± 2 K in all cases. Details of insulation and the temperature profiles are given in Appendix A1.2. The *"Gold" transparent furnace* was monitored by a *type K thermocouple* which was calibrated against mercury-in-glass thermometers (including an exposed stem-end correction). The type K thermocouple was connected directly to a commercial device containing linearization circuits and a cold junction correction. The readout was directly in °C. Similarly a 40 mm temperature profile plateau with variation ± 2°C was generated at set temperatures 170 to 450°C and again illustrated in Appendix A1.2.

2.2 Purification of Gases

Purification of rare gases, argon and helium were achieved by passage through a *commercial rare gas purifier* (RGP), which included a titanium getter operating at 700°C to remove O_2 and N_2, copper oxide at 450°C to remove H_2, hydrocarbons and CO and molecular sieves to remove CO_2 and H_2O. Further purification involved passage through more molecular sieves and hot copper turnings maintained at 450°C to remove water vapour and oxygen respectively, see figure 2.3. Nitrogen gas was purified by passage through a column containing molecular sieves and a column of copper turnings only. Hydrogen was introduced in a similar fashion following purification via a palladium diffuser. A third gas inlet line was available for the introduction of hydrogen chloride dried via a column of magnesium perchlorate. Molecular sieves and magnesium perchlorate were regenerated at regular intervals by heating under vacuum at 170°C or 150°C respectively for 24 hours table 2.2 indicates the level of manufacturers' impurities of the gases (< 20 ppm(v)) and materials used in thesis.

2.3 Mass Flow Controllers

Fixed gas flow rates were obtained by using *mass flow controllers* (MFC) which were factory-calibrated to an accuracy of ± 1% of the full scale readout, displayed on and driven by a *MFC command box*. For inert gases, typical flow rates were between 70 to 100 $cm^3\ min^{-1}$ and for reactive gases (hydrogen chloride), between 5.0 to10.0 $cm^3\ min^{-1}$. The MFC had internal compensating circuitry to correct the flow

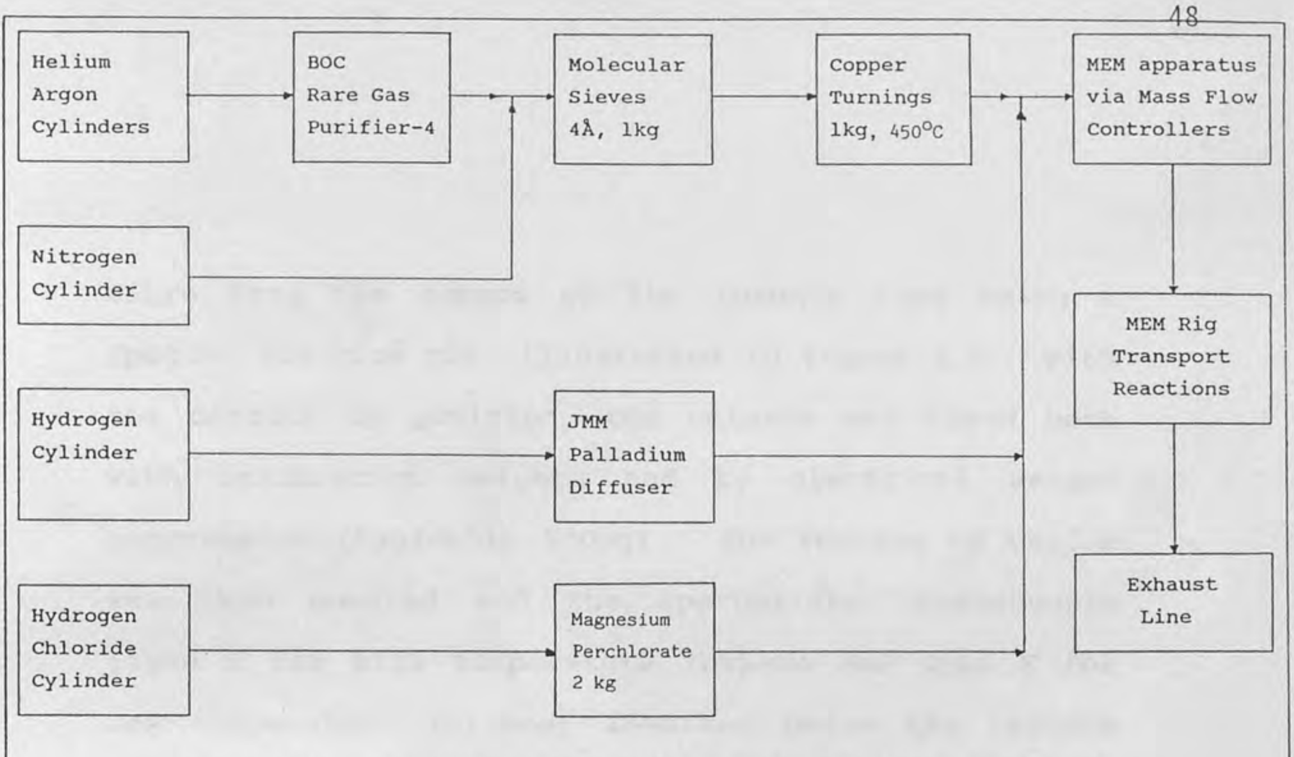


Figure 2.3. Purification flow system of Gases used in MEM experiments

rates to 0°C and 1.0 atm. The normal operating conditions of the MFC were at ambient temperature (5 to 40°C) and a gas differential pressure of the inlet feed line and outlet line of between 0.3 to 3.0 atm. Temperature coefficient and pressure coefficient corrections for the MFC were therefore not necessary.

2.4 Experimental Procedure

The capsule was cleaned in a mixture of concentrated nitric and sulphuric acids (1:1 v/v) for 24 hours, rinsed thoroughly in distilled water and dried under vacuum at 170°C for several hours before any sample of interest was loaded into it. Before the microbalance was calibrated with a *100 mg class E2* calibration weight, the machine was switched on for at least 24 hours to stabilize its electrical components to the working ambient environment. The silica fibre was suspended from one arm of the microbalance and the capsule was then introduced onto the lower hook of the fibre from the bottom of the furnace tube using a special "suction gun" illustrated in figure 2.4. With the capsule in position, the balance was tared both with calibration weights and by electrical weight suppression (typically 500mg). The furnace of choice was then mounted and the appropriate thermocouple (type R for high temperature furnace and type K for low temperature furnace) inserted below the capsule and the glassware connected to the vacuum line and gas outlet.

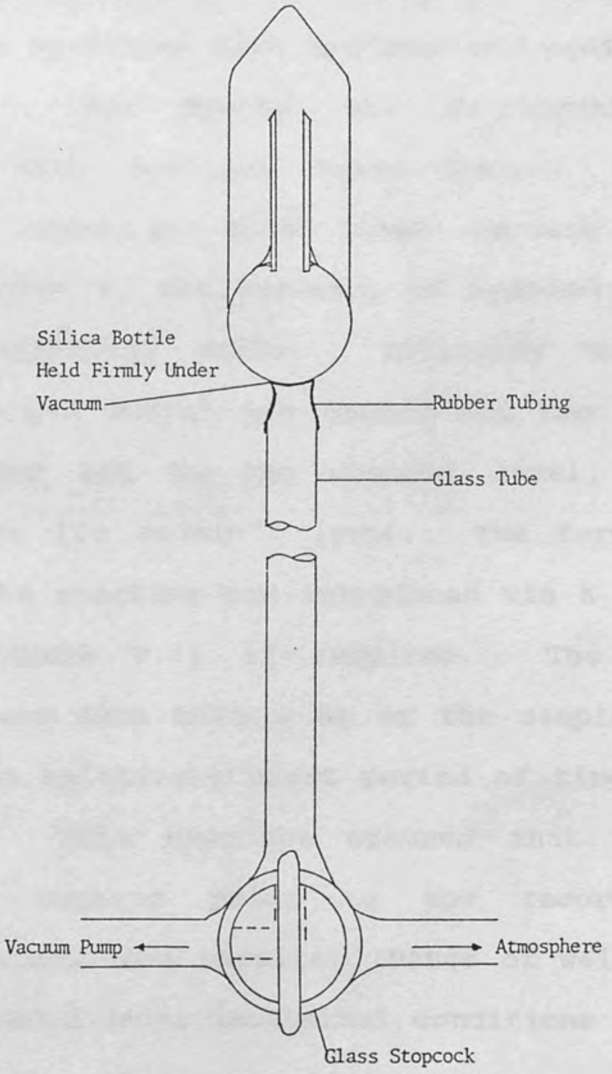


Figure 2.4 MEM Suction Gun Used to Locate Silica Bottle onto Fibre Hook

Once assembled, the apparatus was evacuated to 5 x 10^{-2} mmHg or better, firstly through the gas inlets and then also through the bottom of the furnace tube. Evacuation through the bottom of the furnace tube was delayed until low pressure has been attained, otherwise turbulence would seriously buffet the bottle and cause the suspension fibre to break. After filling with purified argon to atmospheric pressure, the system was next leak tested using a *gas leak detector* or soapy water. Evacuation was repeated and the apparatus re-filled with hydrogen and again tested as before. The system was re-evacuated and back-filled with hydrogen twice more. Hydrogen filling was used at this stage because heating metallic samples in the presence of hydrogen usually removes adventitious oxide. Following the final filling, the gas outlet was opened and the hydrogen flow rate was set to the desired level, usually between 70 to 100 cm^3min^{-1} (stp). The furnace was heated and the reactive gas introduced via a separate line (see figure 2.1) if required. The furnace temperature was such that $\simeq$ 5% of the sample weight was lost in a relatively short period of time (ca. a few hours). This exercise ensured that a clean surface was exposed prior to the recording of definitive weight loss results. Rates of weight loss ($\mathring{\omega}$) were recorded under isothermal conditions over the chosen temperature range taking several data (two or more) measurements for any one temperature to check reproducibility. The temperature sequence depended upon the material being studied. In general however, after recording points over a selected range, it was desirable to repeat points in this range chosen at random. If reproducibility of $\overset{\circ}{\omega}$ was not observed, this suggests either a non-equilibrium process and or the development of a kinetic barrier to material transport e.g. an oxide film on the surface of the sample. Irrespective of the number of reactions involved in the experiment understudy and its detailed theory, a plot of $(-)\ln\overset{\circ}{\omega}$ vs. $1/T$ was usually linear which provided a quick and convenient check on the progress of the experiment and quickly identified "rogue" points.

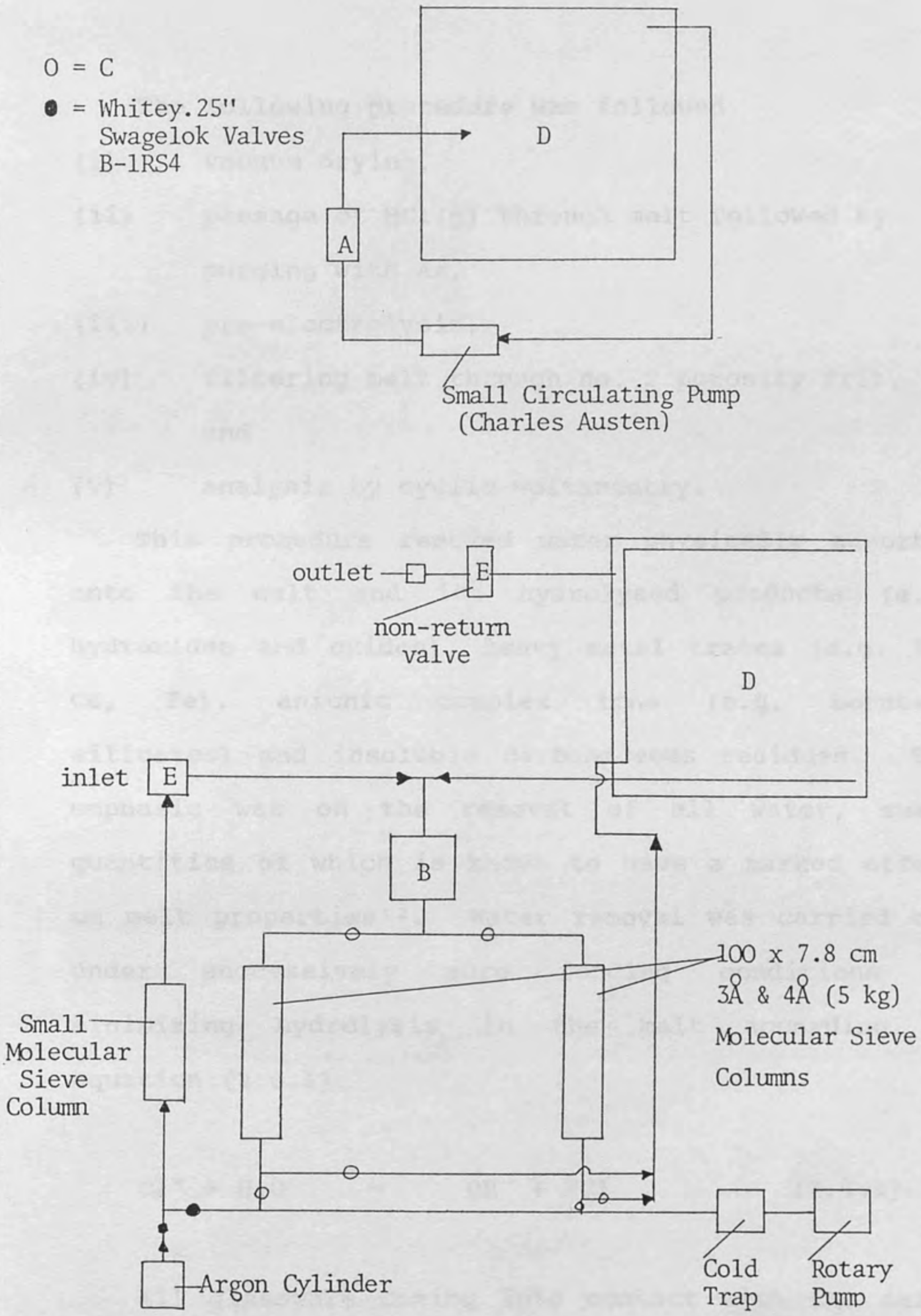
To ensure the microbalance remained in a non-corrosive environment, inert carrier gas was flowed via the upper gas inlet (figure 2.1), whilst if required the reactive gas hydrogen chloride was introduced below the constriction through the lower inlet. A positive pressure of greater than 3 mmHg above atmospheric pressure was maintained in the rig during operation precluding ingress from the surrounding atmosphere. A *Fortin barometer* was used to measure atmospheric pressure in the Laboratory Complex during MEM experiments.

2.5 Dry Handling Facilities

The dry-box used in this work was an upgraded *Linott Mark 1 twin-glove box.* Using 3Å and 4Å molecular sieves to dry re-circulated argon, the moisture level in the box was reduced to 5 ppm(V) H_2O. The system is sketched in figure 2.5 and its associated hardware listed in table 2.3. A positive pressure of 4 mmHg above atmospheric pressure was maintained in the box to preclude leakage inwards from the surrounding atmosphere. With the glove ports closed it was found that water vapour seeped through and collected inside the gloves during periods of non-usage. This caused initial unnecessary damping to the atmosphere ($>$ 100 ppm(V) H_2O) when used. To prevent this diffusion of vapour through the gloves, the glove doors were permanently removed enabling the circulating system to purge the box and the glove volume continuously. Some commercial designs have separate purging systems for this purpose.

2.6 Purification of Analar Zinc Chloride

Purification of Analar Zinc Chloride was undertaken at the department of Metallurgy and Material Science, Imperial College with the advice of Professor Inman and Drs. Dudley and Duan.



A) Moisture Meter, B) Compressor Pump, C) Ball Valves,
D) Dry Box, and E) Solenoid Valve

Figure 2.5 Block Diagram of Gas Circulating System to Dry-Box

The following procedure was followed

(i) vacuum drying,

(ii) passage of HCl(g) through melt followed by purging with Ar,

(iii) pre-electrolysis,

(iv) filtering melt through no. 2 porosity frit, and

(v) analysis by cyclic voltammetry.

This procedure removed water physically adsorbed onto the salt and its hydrolysed products (e.g. hydroxides and oxides), heavy metal traces (e.g. Pb, Cu, Fe), anionic complex ions (e.g. borates, silicates) and insoluble carbonaceous residues. The emphasis was on the removal of all water, small quantities of which is known to have a marked effect on melt properties[12]. Water removal was carried out under successively more forcing conditions so minimizing hydrolysis in the melt according to equation (2.6.1)

$$Cl^- + H_2O \quad = \quad OH^- + HCl \qquad (2.6.1)$$

All glassware coming into contact with the salt, i.e. melt receiver, filter tube and ampoules, were soaked in 1:1 (v/v) concentrated sulphuric/nitric acid baths for 24 hours, washed with distilled water and acetone and finally dried at approximately 200^{o}C for

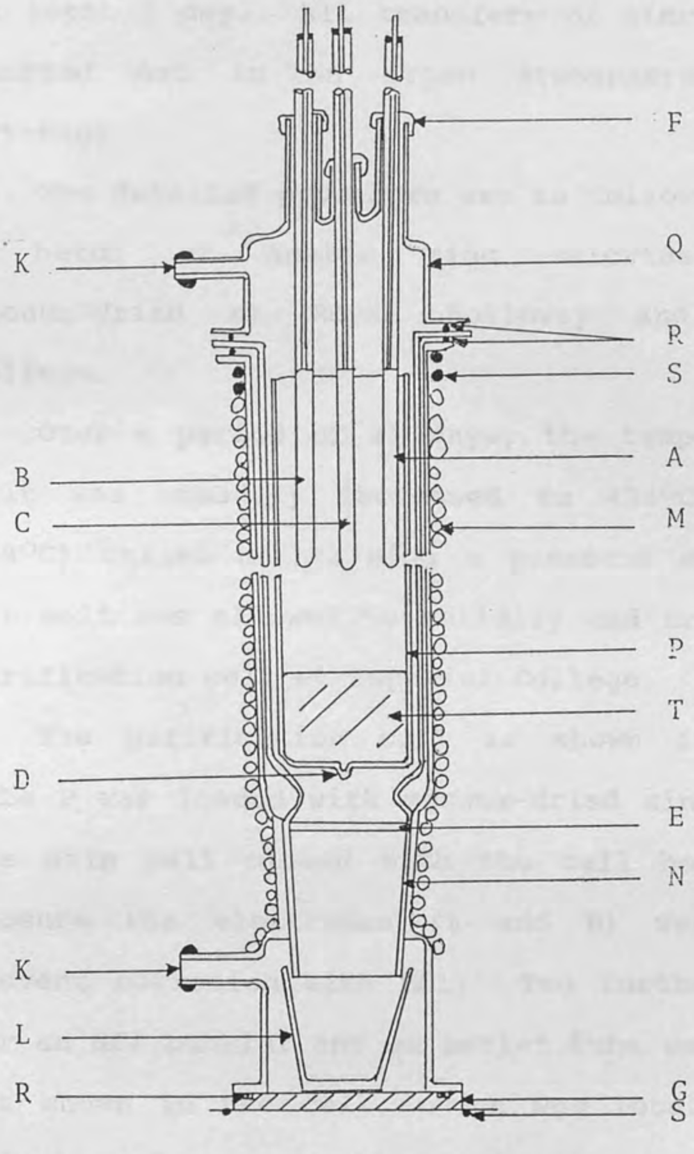


Figure 2.6 Apparatus for the Purification of Zinc Chloride

A, Anode; B, Cathode; C, Pyrex breaker rod; D, Breakable glass dimple; E, glass sinter (no. 2 porosity); F. Quickfit screw thread joint and cap SQ13; G, Brass plate; K, S29 Ball to vacuum system; L, Pyrex receiver; M, Heating element; N, B45 of inner filter tube; P, Inner Pyrex tube; Q, Pyrex cell head on F.G. 70 flange; R, "O" rings; S, Cooling water system; T, Zinc chloride.

at least 1 day. All transfers of zinc chloride were carried out in an argon atmosphere (dry-box or dry-bag).

The detailed procedure was as follows:
A batch of Analar zinc chloride (500g) was vacuum-dried at Royal Holloway and Bedford New College.

Over a period of 21 days, the temperature of the salt was steadily increased to 424°C (mp $ZnCl_2 \simeq$ 318°C) whilst maintaining a pressure of $\leqslant$ 0.1 mmHg. The melt was allowed to solidify and transferred to a purification cell at Imperial College.

The purification cell is shown in figure 2.6. Tube P was loaded with vacuum-dried zinc chloride and the main cell closed with the cell head Q. Before closure the electrodes (A and B) were removed to prevent corrosion with HCl. Two further entry ports for an HCl bubbler and an outlet tube were present but not shown in the cell, which was located behind the illustrated entry ports in figure 2.6. The cell was evacuated using a two stage rotary pump to a pressure below 0.04 mmHg. This initial pumping took approximately 24 hours and was essential to reduce the adventituous water content to a minimum before heating commenced. The temperature was raised in several stages to 340°C with continuous pumping.

Hydrogen chloride gas, dried via molecular sieves

AW100 and activated charcoal was introduced into the system, which had been purged to 1 atmosphere with dried argon. The gas was first flushed over the surface of the melt and then the gas dispersed through the melt via a bubbler frit; after about 35 minutes the HCl stream was discontinued and the melt purged with Ar for 55 minutes. HCl was passed through the system to remove OH^- and O^{2-}, the major products of hydrolysis.

$$HCl(g) + OH^-(melt) = Cl^-(melt) + H_2O(g) \quad (2.6.2)$$

$$2HCl(g) + O^{2-}(melt) = 2Cl^-(melt) + H_2O(g) \quad (2.6.3)$$

Unfortunately Cl_2 was not available to bubble through the melt at this stage to remove OH^-.

$$2Cl_2(g) + 2OH^-(melt) = 2HCl(g) + O_2(g) + 2Cl^-(melt) \quad (2.6.4)$$

The pre-electrolysis electrodes (cathode:stainless steel, anode:vitreous carbon (boiled in conc.HCl, washed with distilled water and baked at 200°C for 24 hours)) were quickly introduced through the cell head under high argon flow and a constant voltage (1.5V) supply connected. The anode was lowered into the melt followed by the cathode (to ensure cathodic protection of the stainless steel). The pressure in the cell was immediately reduced to aid stirring by expanding the evolving anodic gases and hence avoid polarization at the anode. The initial current was 2 to 3 mA and fell to zero within an hour. This technique[13] will remove electroactive species that are dissolved in the melt and that have a decomposition potential within the "potential window" of the $ZnCl_2$ melt (or solvent). For $ZnCl_2$, the cathodic limit is $Zn^{2+} + 2e \rightarrow Zn$ and the anodic limit is $Cl^- \rightarrow 0.5Cl_2 + e^-$. Thus, metals less electropositive than Zn e.g. Cd,Fe,Pb will be removed by deposition on the cathode, but the more electropositive metals e.g. Ca,Mg,Al will not be removed. Similar consideration applys to the removal of the negative ions although the anodic limit for $ZnCl_2$ is not so limiting as F^- is probably the only impurity of any significance whose deposition potential is more anodic. When applying this method, the electrode materials must be chosen with care[13] and continuous pumping maintained throughout to enhance stirring and remove anodic gases so reducing anodic polarization.

The dimple D was broken using the rod C, and with a suitable argon gas pressure above the frit and reduced pressure below the frit, the melt was filtered through into the receiver L. However when the dimple D was broken the rod C accidentally punctured the glass filter frit and some insoluble products still remained in the melt during electroanalysis. This does not affect the analysis because cyclic voltammetry (CV) only detects electroactive species dissolved in the melt. Because of the contamination of the melt described above, after CV the sample was returned to the filteration apparatus (figure 2.6), pumped down, melted over a period of 5 days and refiltered.

Subdivision of $ZnCl_2$ into Aliquots

The purified batch of $ZnCl_2$ was broken up in the dry-box and quickly put into a closed jar. Each lump of melt was subsequently ground and transferred into a pre-dried ampoule. This allowed closed ampoules to be removed from the dry-box prior to evacuation and sealing. The moisture content of the dry-box (I.C. not RHBNC box) rose from 6 ppm(V) to 150 ppm(V) of water during this procedure (the unit is part per million by volume - 10 ppm(V) corresponds to a partial pressure of H_2O of ca. 0.008 mmHg). This is probably due to diffusion of moisture through the gloves.

Sealing of Ampoules

Figure 2.7 shows the dimensions of the $ZnCl_2$ ampoules used. Five ampoules at the time were taken out of the drybox. Before sealing each was evacuated and heated gently with a luminous flame to remove any moisture contamination.

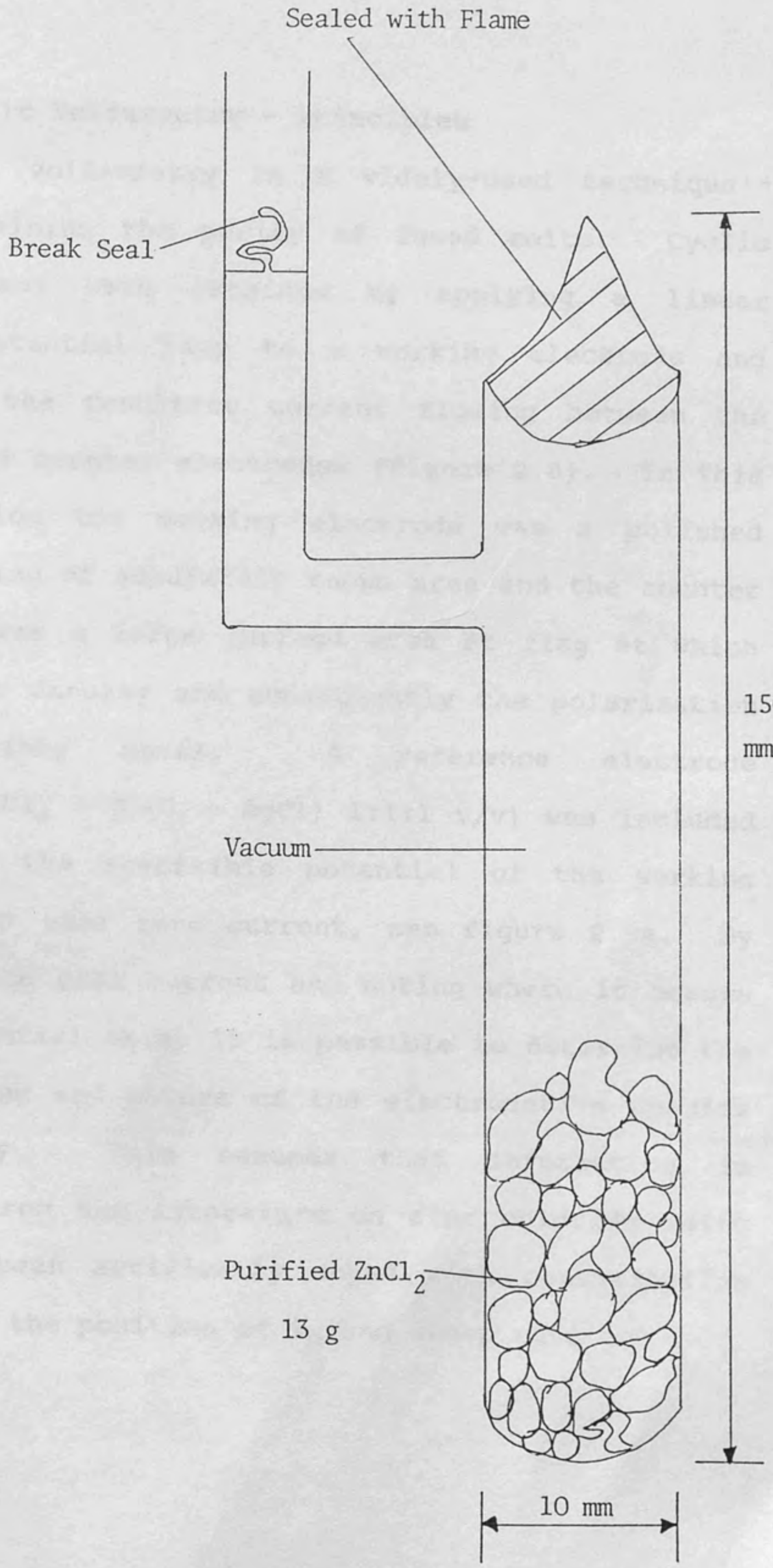


Figure 2.7 $ZnCl_2$ Ampoules

2.7 Cyclic Voltammetry - Principles

Cyclic voltammetry is a widely-used technique[14] for determining the purity of fused melts. Cyclic voltammograms were obtained by applying a linear varying potential ramp to a working electrode and measuring the resultant current flowing between the working and counter electrodes (figure 2.8). In this investigation the working electrode was a polished tungsten disc of accurately known area and the counter electrode was a large surface area Pt flag at which the current density and consequently the polarization is negligibly small. A reference electrode ($Ag/AgCl(ZnCl_2$ + NaCl + AgCl) 1:1:1 v/v) was included to measure the reversible potential of the working electrode at near zero current, see figure 2.9a. By measuring the peak current and noting where it occurs on the potential axis, it is possible to determine the concentration and nature of the electroactive species respectively. This assumes that information is available from the literature on zinc chloride melts that have been artifically doped with contaminating species and the position of i_p and sweep rate noted.

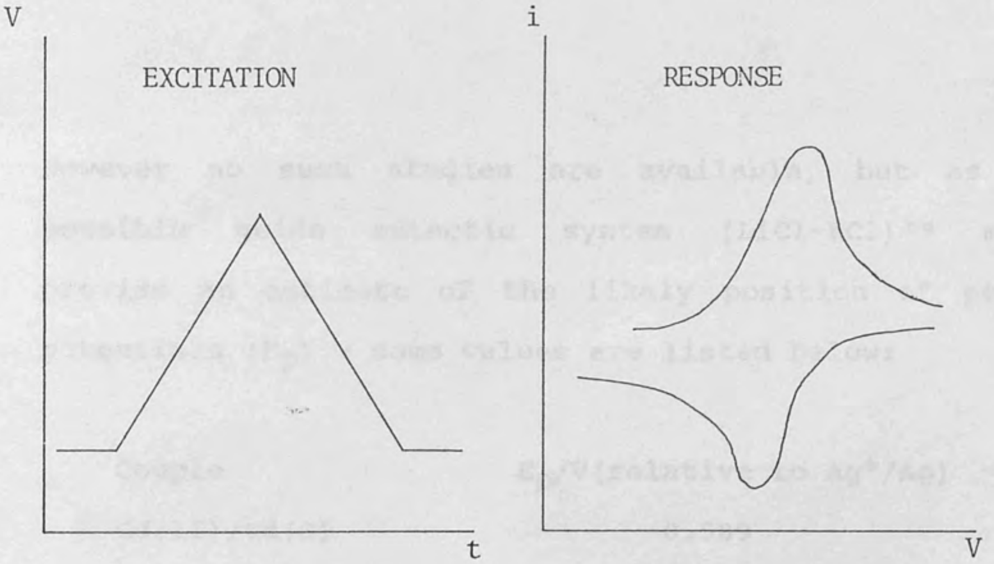


Figure 2.8a Cyclic Voltammetry - Excitation and Response for the Reversible Deposition of a Soluble Product

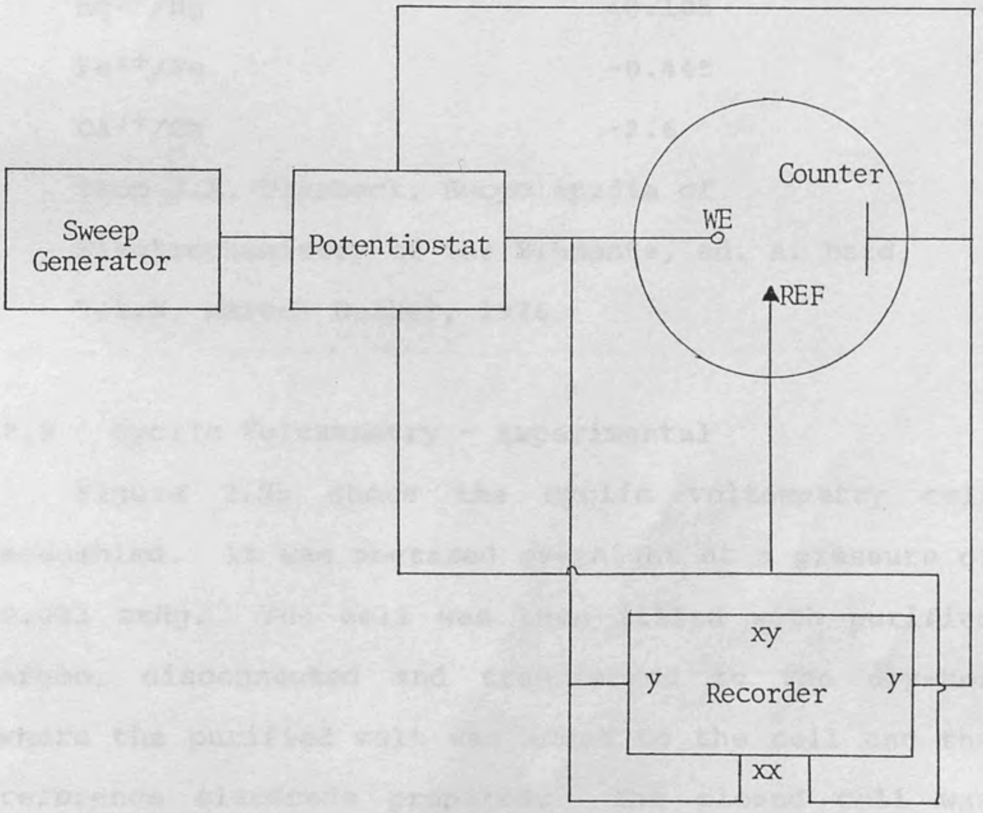


Figure 2.8b Schematic Diagram of Cyclic Sweep Circuit

However no such studies are available, but as a possible guide eutectic system (LiCl-KCl)[14] may provide an estimate of the likely position of peak potentials (E_p) - some values are listed below:

Couple	E_p/V(relative to Ag^+/Ag)
Cd(II)/Cd(O)	-0.589
Pb(II)/Pb(O)	-0.374
$HCl(g)/H_2(g)/Pt$	-0.017
$Cl_2(g),C/Cl^-$	1.033
$Br_2(g),C/Br^-$	0.857
Zn^{2+}/Zn	-0.839
Hg^{2+}/Hg	+0.105
Fe^{2+}/Fe	-0.445
Ca^{2+}/Ca	-2.6

from J.A. Plambeck, Encyclopedia of Electrochemistry of the Elements, ed. A. Bard, Vol.X, Marcel Dekker, 1976.

2.8 Cyclic Voltammetry - Experimental

Figure 2.9b shows the cyclic voltammetry cell assembled. It was degassed overnight at a pressure of 0.023 mmHg. The cell was then filled with purified argon, disconnected and transferred to the dry-box where the purified melt was added to the cell and the reference electrode prepared. The closed cell was then reconnected to the vacuum line and evacuated overnight. Argon was introduced into the cell, providing a small flow at a slight positive pressure before melting the salt. The electrodes were then lowered into the melt and voltammetry started.

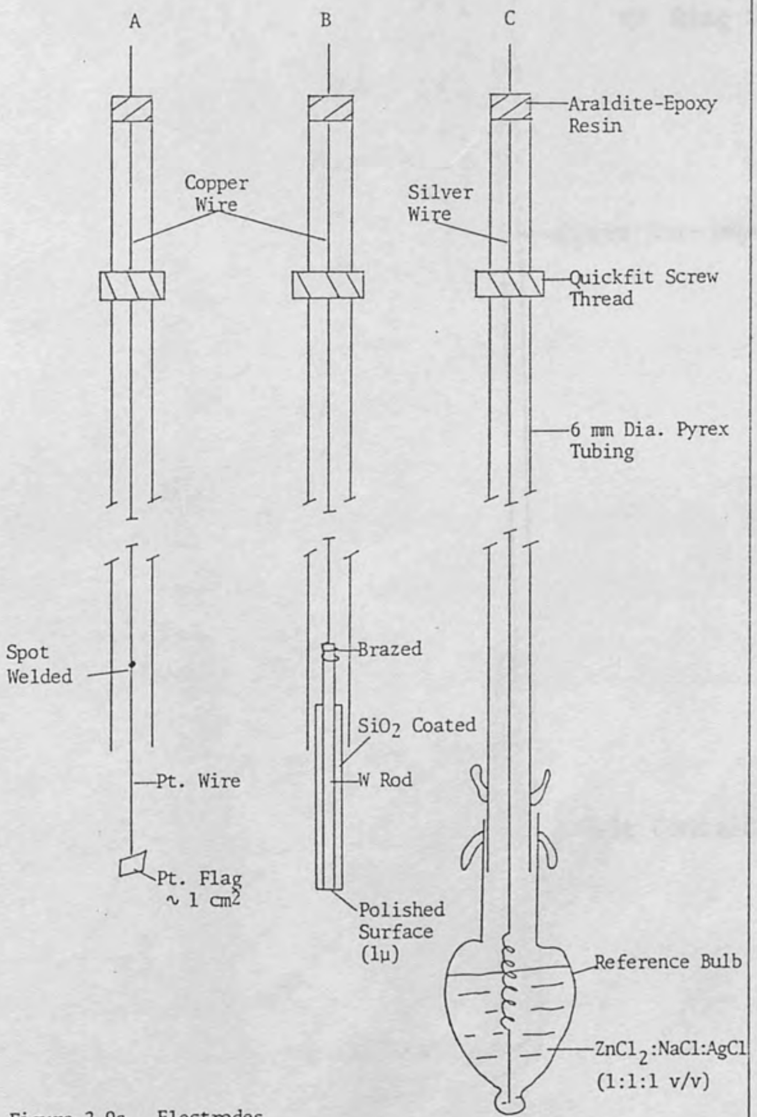


Figure 2.9a Electrodes

A. Counter Electrode
B. Working Electrode
C. Reference Electrode

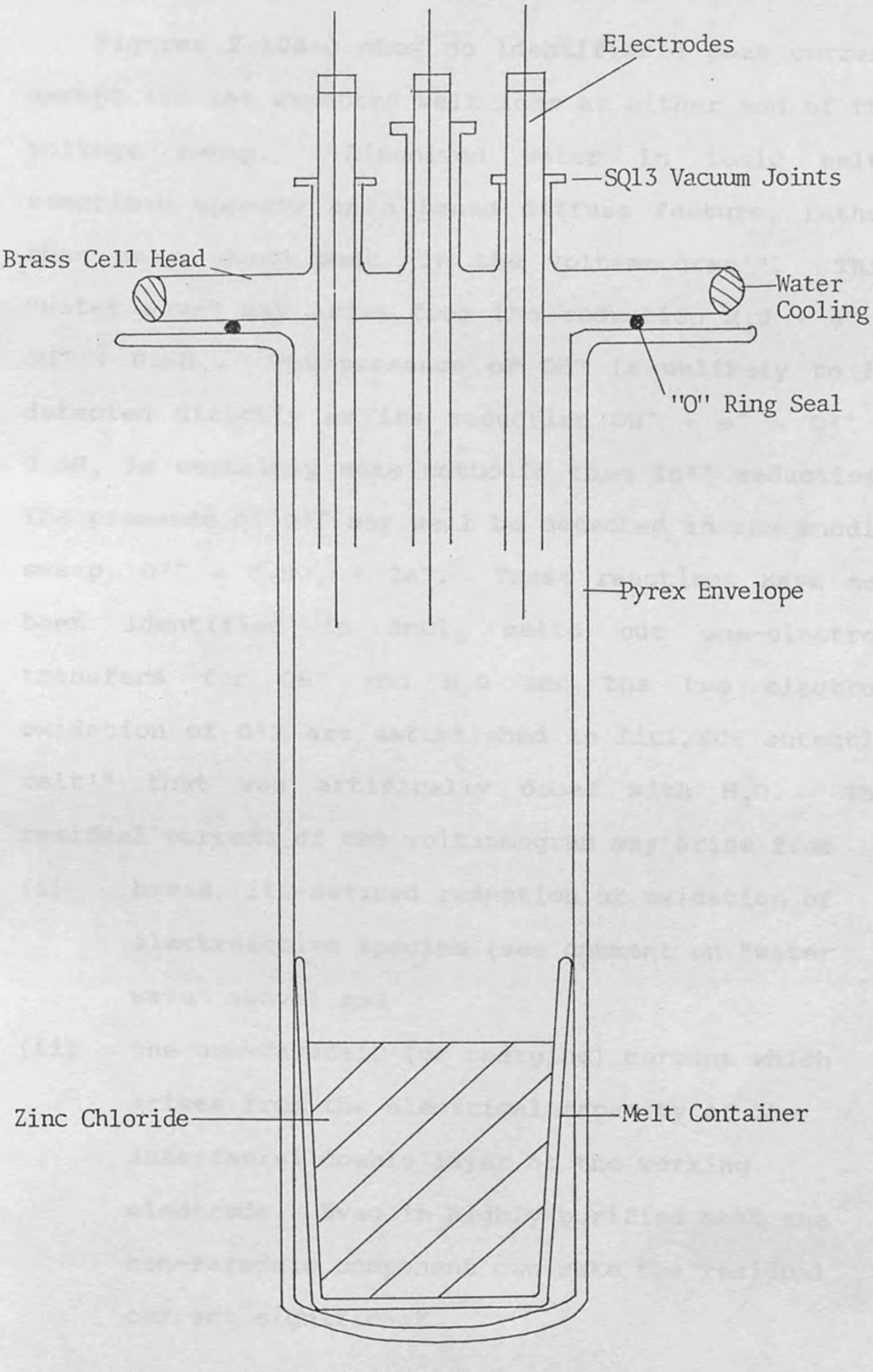


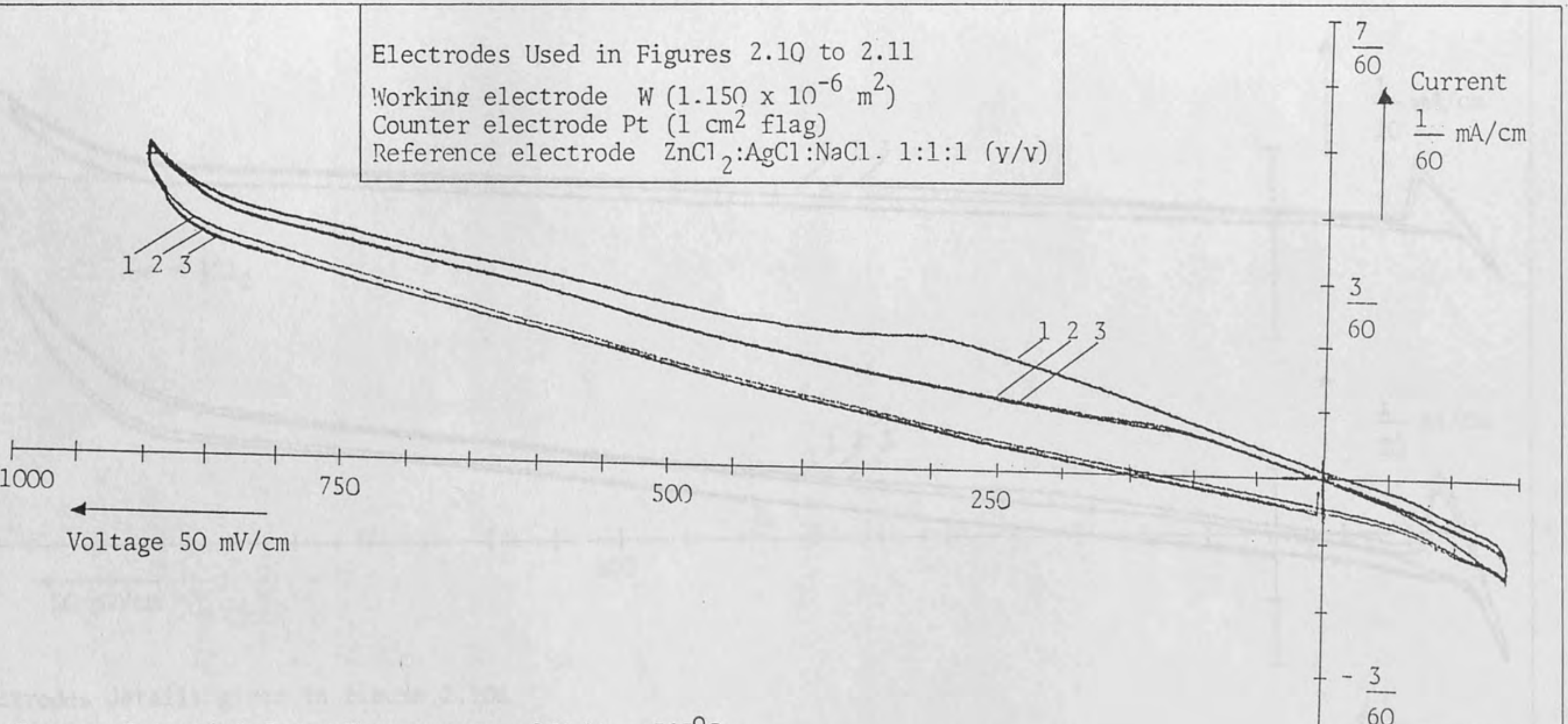
Figure 2.9b Electrochemical Cell

In and outlet for vacuum and argon line and thermocouple in Pyrex tubing via brass-cell head not shown for clarity.

Figures 2.10a-c show no identifiable peak current except for the expected melt ions at either end of the voltage sweep. Dissolved water in ionic melts sometimes appears as a broad diffuse feature, rather than as a sharp peak, in the voltammogram[14]. This "water wave" may arise from the reduction $H_2O + e^- \rightarrow OH^- + 0.5H_2$. The presence of OH^- is unlikely to be detected directly as its reduction $OH^- + e^- \rightarrow O^{2-} + 0.5H_2$ is certainly more cathodic than Zn^{2+} reduction. The presence of O^{2-} may well be detected in the anodic sweep, $O^{2-} \rightarrow 0.5O_2 + 2e^-$. These reactions have not been identified in $ZnCl_2$ melts but one-electron transfers for OH^- and H_2O and the two electron oxidation of O^{2-} are established in LiCl/KCl eutectic melt[15] that was artifically doped with H_2O. The residual current of the voltammogram may arise from

(i) broad, ill-defined reduction or oxidation of electroactive species (see comment on "water wave" above) and

(ii) the non-Faradaic (or charging) current which arises from the electrical capacity of the interfacial double layer at the working electrode. Even in highly purified melt the non-Faradaic component can make the residual current significant.



Electrodes Used in Figures 2.10 to 2.11

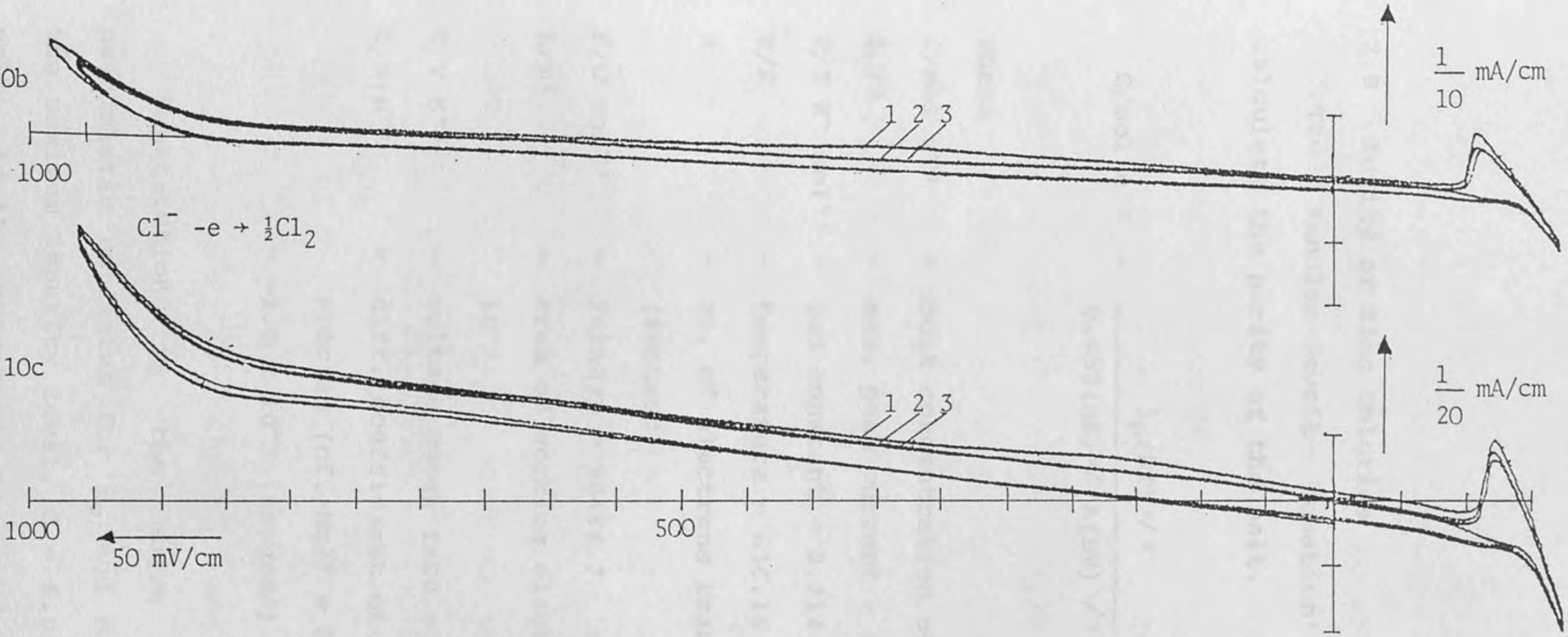
Working electrode W (1.150 x 10^{-6} m^2)
Counter electrode Pt (1 cm^2 flag)
Reference electrode $ZnCl_2$:AgCl:NaCl. 1:1:1 (v/v)

Current Potential Data: Temperature of Melt = 363°C.
Residual Voltage (E_R) = 1mV, Sweep Rate = 50 mV/sec

Figure 2.10a Cyclic Voltammogram of Purified Zinc Chloride

Fig. 2.10b

Fig. 2.10c



Electrodes details given in figure 2.10a

Current Potential Data: Temperature of Melt = 363°C

Residual Voltage (E_R) = 1 mV Sweep Rate = 50 mV/sec

Figures 2.10b and 2.10c Cyclic Voltammogram of Purified Zinc Chloride

2.9 Purity of Zinc Chloride

The Randles-Sevcik equation[16] was used to calculate the purity of the melt.

$$C/\text{mol m}^{-3} = \frac{i_p(RT)^{1/2}}{0.452(nF)^{3/2}A(DV)^{1/2}} = 6.05 \qquad (2.9.1)$$

where

$C/\text{mol m}^{-3}$ = bulk concentration of species

i_p/A = max. peak current = 9.166×10^{-6}

$R/\text{J K}^{-1}\text{mol}^{-1}$ = gas constant = 8.314

T/K = temperature = 636.15

n = no. of electrons transferred = 1 (assumed)

$F/\text{C mol}^{-1}$ = Faraday = 96486.7

A/m^2 = area of working electrode = 1.1499×10^{-6}

$V/\text{V S}^{-1}$ = voltage sweep rate = 50×10^{-3}

$D/\text{m}^2\text{s}^{-1}$ = diff. coefficient of electroactive species (cf. $Mg^{2+} = 5.2 \times 10^{-9} \text{m}^2\text{s}^{-1}$)
= 1.0×10^{-9} (assumed)

Substitution in the above equation (using pessimistic estimates for i_p and n selected) yields the maximum impurity level, $C = 6.05$ mol m^{-3} or 0.03 mol%. If the impurity is assumed to be only H_2O then $C(H_2O) = 1.91 \times 10^{-3}$ wt%. While these results are encouragingly low, the most disappointing feature of this analytical procedure is the inability to detect a peak current for OH^- as it presumably lies outside the $ZnCl_2$ "potential window". However this may be of no consequence as it is known[14,18] that in the LiCl/KCl eutectic melt (mp 450°C) the equilibrium $2OH^- = H_2O(g) + O^{2-}$ lies far to the right, meaning that OH^- may be detected as O^{2-} and H_2O.

To obtain some estimation of the sensitivity of the technique Analar Zinc Chloride was analysed under identical conditions except the temperature was 6K higher (642.15K). This initial cyclic voltammogram (figure 2.11a) for which the sample was heated and evacuated showed some evidence of impurities at +0.9V to +0.4V (wave 1) and at 0.0V to 0.25V (wave 2) vs. Ag/Ag^+ reference electrode ($ZnCl_2$:AgCl:NaCl = 1:1:1 v/v). Wave 2 appears to be an irreversible cyclic sweep in constrast to the conventional anodic and cathodic reversible reaction of a metal ion (Zn^{2+}) as shown in figure 2.10b. Hence by evacuating $ZnCl_2$ overnight and raising the temperature from 298K to 642K the purity of the melt, using the information obtained from manufacturer's purity specification and using equation (2.9.1) on figure 2.11a, rose from 98 → 99.9 mol%. Exposing this evacuated pre-dried melt now to a steady stream of laboratory air, these two current waves intensified, elongated and masked all other waves. Their intensities steadily increased with time whilst drawing air over the melt (figure 2.11b) and not surprisingly decreased with time when the system was re-evacuated (figure 2.11c). Further exposure of air at a more rapid rate resulted in wave 2 decreasing as wave 1 steadily increased (figure 2.11d - 2.11f). Under these conditions moisture and oxygen are the only sources of impurity.

A general overall mechanism may be as follows:

$$ZnCl_2(\ell) + 2H_2O(g) \quad = \quad [ZnCl_2 + 2H_2O](soln) \qquad (2.9.2)$$

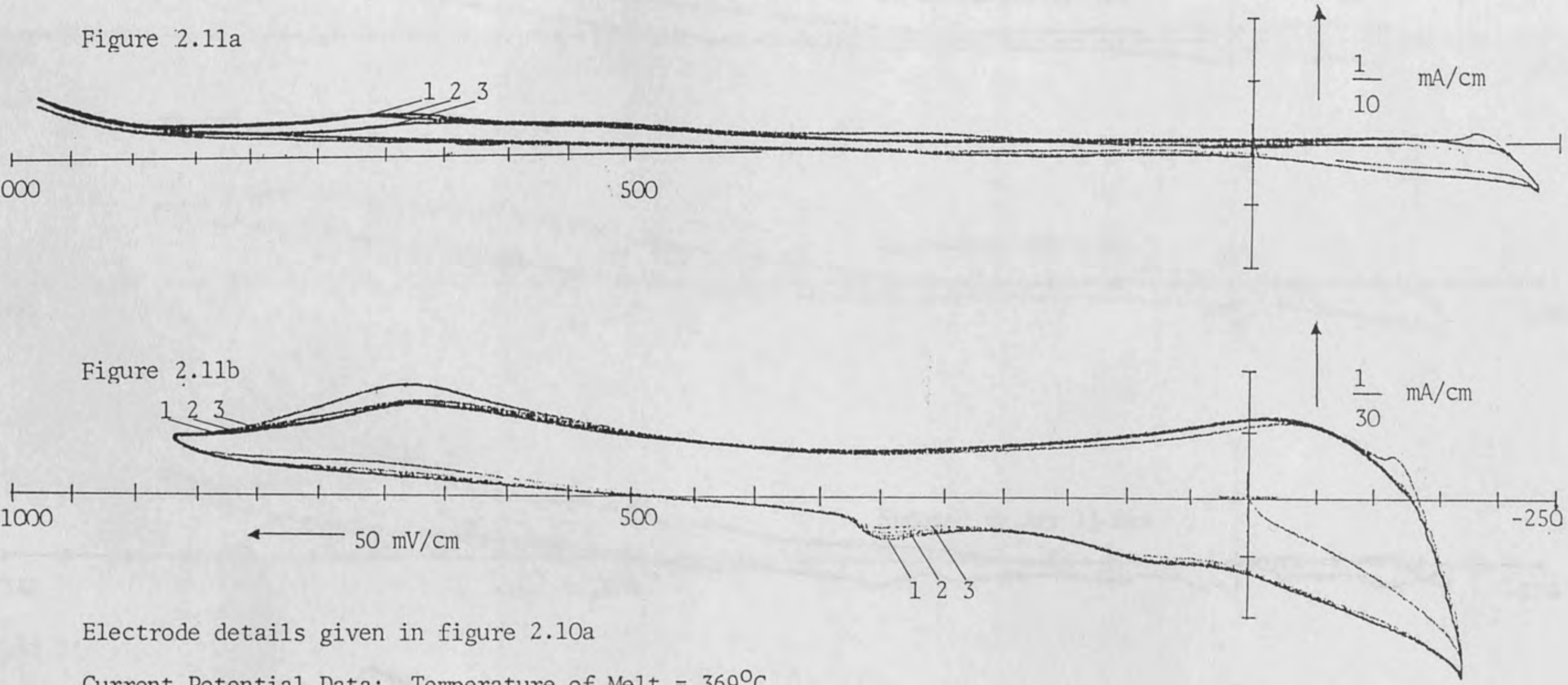
$$\Big\downarrow \begin{array}{l}\text{Fast}\\ \text{Hydrolysis}\end{array}$$

$$[ZnO + H_2O](complex) \underset{\text{slow}}{=} Zn(OH)_2(soln) + 2HCl(g) \uparrow$$

Initially $H_2O(g)$ dissolves to a slight extent in the melt (to $\leqslant$ 0.1 mol%). Hydrolysis may be rapid at the melt temperature causing a decrease in the size of the "water wave" (wave 2) and an increase in the (unseen) OH^- feature presumably outside the "potential window" of $ZnCl_2$. Subsequently a slow step converts the OH^- to O^{2-} complex, so explaining the steady build up of the "oxide feature" - wave 1 (see figure 2.11d - 2.11f). The presence of wave 1 indicating "oxide" in the melt, appears to inhibit further uptake of moisture as wave 2 the "water wave", in the successive voltammograms showing its steady decline.

Figure 2.11a

Figure 2.11b



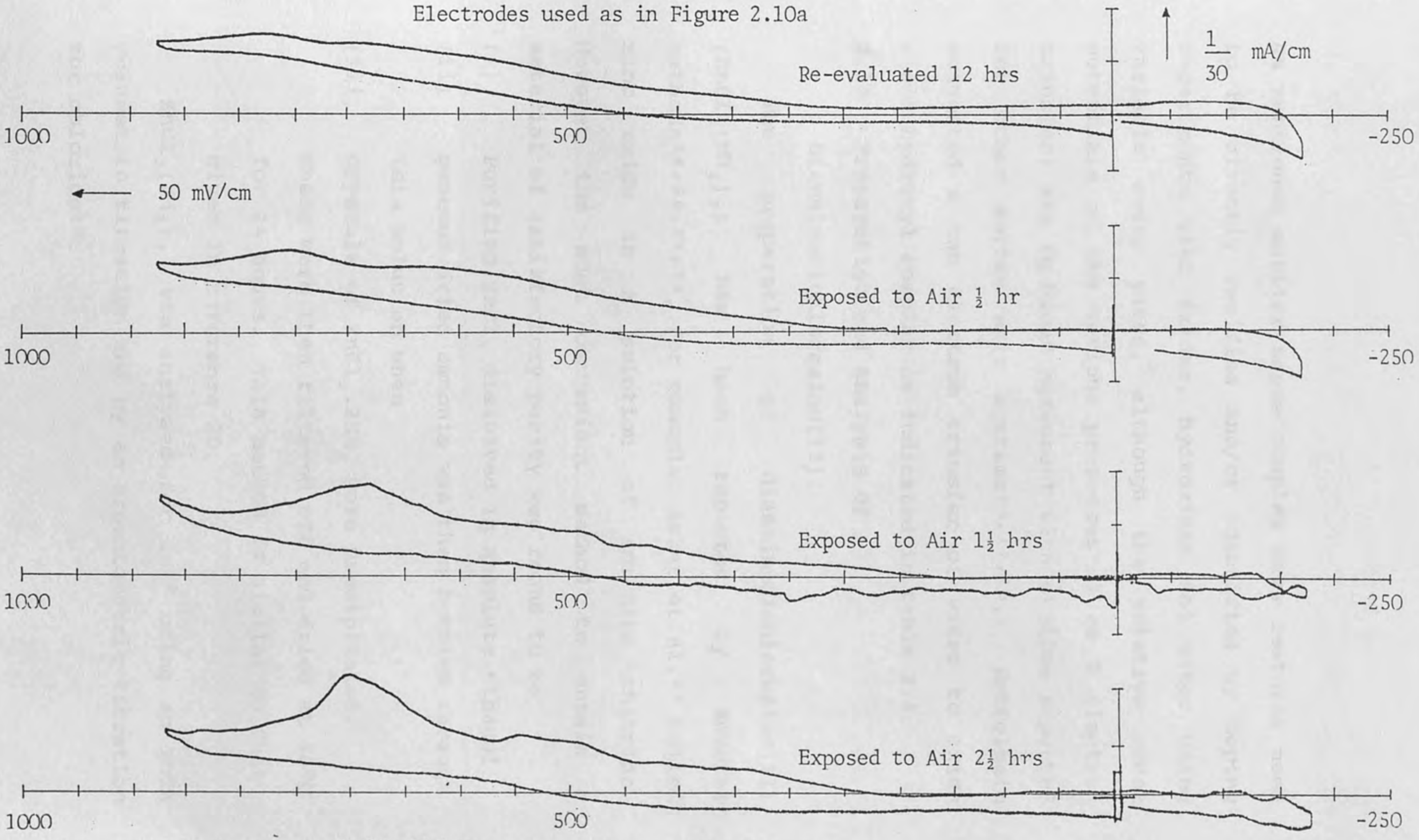
Electrode details given in figure 2.10a

Current Potential Data: Temperature of Melt = 369^{o}C

Residual Voltage (E_R) = 1 mV, Sweep Rate = 50 mV/sec

Figure 2.11a and 2.11b Cyclic Voltammogram of Analar Zinc Chloride

Condition of Melt a) Vacuum Melted then filled with Ar, b) Exposed to Air for 1.5 hrs.



Figures 2.11c to 2.11f Cyclic Voltammogram of Analar Zinc Chloride

As mentioned earlier these complex wave features need to be directly verified and/or identified by doping experiments with oxides, hydroxides and water using variable sweep rates, although the relative redox potentials of the various processes (1 or 2 electron transfer) are in broad agreement with studies reported for other molten salt systems[14,17,18]. Bettelheim suggested a two electron transfer of water to oxide via a hydroxyl complex as indicated in table 2.4.

2.10 Preparation and Analysis of Diamminedichlorozinc(II).

The preparation of diamminedichlorozinc(II) ($ZnCl_2(NH_3)_2$) has been reported by several methods[19,20,21,22], for example, Asker et al.[21] boiled zinc oxide in a solution of ammonium chloride. However the most convenient method to obtain a material of satisfactory purity was found to be

(i) Purified $ZnCl_2$ dissolved in absolute ethanol

(ii) gaseous dried ammonia was then bubbled through this solution when

(iii) crystals of $ZnCl_2.2NH_3$ were precipitated. These were then filtered off and dried at 50°C for 24 hours. This method is similar to that given in reference 20.

$ZnCl_2(NH_3)_2$ was analysed for Zn^{2+} using an EDTA volumetric titration and by an argentometric titration for chloride[23].

The results were as follows:

$ZnCl_2(NH_3)_2$	%Zn	%Cl
Found	38.8_7	41.5_5
Theoretical	38.38	41.63

The agreement between the calculated and experimental analysis results is satisfactory.

Table 2.1

Model Type, Model Serial No.,
Manufacturer's Specifications and Addresses.

Recording microbalance

Cahn R100 Electrobalance, #5050/30324, Cahn Instruments, Inc., 16207 S. Carmenita Road, Cerritos, CA 90701, USA.
UK Agents: Scientific and Medical Products Ltd., Shirley Institute, Didsbury, Manchester, M20 8RX.

Anti-static work station kit and tray

#550-022 and #550-151, RS Components Ltd., The Fairway Estate, Green Lane, Hounslow, Middlesex, TW4 6BU.

Radioactive ionizing unit

Strontium 90β 0.2 μCi, Panax.
Address unknown

Cont.

Table 2.1 (cont.)

Demountable tube furnace

Electric heating unit, # 50142/1718-KSP,
240W, Lindberg International Operations,
Hubbard Street, Chicago, IL60612, USA.
UK Agents: Arnold R. Horwell Ltd., 73,
Maygrove Road, West Hampstead, London,
NW6 2BP.

Linear temperature variable rate programmer

LVP/CC20/R, mark III, Stanton Redcroft,
Copper Mill Lane, London, SW17 OBN.

Cold junction reference compensator

Type RJRS Mains 240V, Cropico Ltd.
UK Agents: Croydon Precision Instrument Co.,
Hampton Road, Croydon, CR9 2RU.

Digital voltmeter

Muitimeter # 1905a, Thurlby Electronics Ltd.,
New Road, St. Ives, Huntington, Cambs.,
PE17 4BG.

Cont.

Table 2.1 (cont.)

Ceramic wool fibre

For Lindberg furnace - standard thickness and density 13 mm x 48 kg m^{-3}.

For Trans Tempfurnace - standard thickness and density 25 mm x 96 kg m^{-3} with hardener solution added.

Triton Kaowool ceramic fibre blanket,
Morganite Ceramic Fibres Ltd., Tebay Road,
Bromborough, Wirral, Merseyside, L62 3PH.

Gold transparent furnace

Internal diameter and length 65 mm x 406 mm, 10A power rating. TransTemp, 155 6th Street,
Chelsea, Mass. 02150, USA.

Type K thermocouple and display box

Keithley Model 8712, glass braid sheath;
Keithley, 871 Digital Thermometer Type K,
Keithley Instruments Ltd., 1 Boulton Road,
Reading, Berkshire, RG2 0NL.

Cont.

Table 2.1 (cont.)

Rare gas purifier

BOC RGP4, BOC Special Gases, Great West House, Great West Road, Brentford, Middlesex, TW8 9DQ.

Palladium diffuser

JMM Hydrogen Diffusion Unit, #H28/1, Johnson Matthey Equipment Ltd., South Way, Exhibition Grounds, Wembley, HA9 0HW.

Mass flow controller (MFC) and
MFC Command box

#AFC 261 for HCl, #AFC 260 for all other gases, #ASM Readout box 6, Advanced semiconductor materials international n.v. (ASM). UK Agents: Epak Electronics Ltd., 34, Holmethorpe Avenue, Redhill, Surrey, RH1 2NB.

Cont.

Table 2.1 (cont.)

100mg E2 ≡ NBS Class S
calibration weight

#ME6528 Mettler calibration weights class E2 tolerance (±0.015mg) according to OIML (Organisation Internatione de Metrologie Légale) No.20/EC.

UK Agents: Gallenkamp, Belton Road,
Loughborough, Leicestershire, LE11 0TR.

Gas leak detector

Gow-Mac gas leak detector #21-212 Std. dc pump w/Audio (220V charger), Gow-Mac Instrument Co., 100 Kings Road, Madison, N.J. 07940, USA.

Fortin barometer

Griffin & George Ltd., Bishop Meadow Road,
Loughborough, Leicestershire, LE11 0RG.

Dry-box with neoprene/butyl/neoprene sandwich gloves (9), Lintott MK1 Twin-Glove Box #814, leak tested at 4.2 SWG for ½ hour and refurbished by Miller Howe Ltd., Watlington Industrial Estate, Watlington, Oxon, OX9 5LU.

Table 2.2

Materials and Manufacturer's Specifications

Gases, Grade, % purity		
Hydrogen	99.99	BOC Ltd., Great West House, Great West Road, Brentford, Middx., TW8 9DQ.
Nitrogen,"White spot"	99.997	
Argon (high purity)	99.999	
Ammonia	99.98	BOC Special Gases, 24 Deer Park Road, London, SW19 3UF.
Helium grade A	99.995	
Hydrogen chloride (electronic grade C)	99.99	Air Products, Doncastle Road, Bracknell, Berks, RG12 4HL.
Materials		
Zinc wire 0 0.250 μm	99.99	Goodfellows Metals Ltd., Ruxley Towers Claygate, Esher, Surrey, KT10 0TS.

Cont.

Table 2.2 (cont.)

Zinc Sulphide gold label, batch 24,462-7,JL0301JK. Molecular Sieves.	99.99	Aldrich Chemical Co. The Old Brickyard, New Road, Gillingham, Dorset, SP8 4SL.
Mercury, trebly distilled		Alexander Pickering & Co. Ltd., 148, Edinburgh Avenue, Trading Estate, Slough, Berkshire. (Co. ceased trading)
Ethanol, absolute quantity AR100	99.7	James Burroughs (FAD) Ltd., 70, Eastways Ind. Parks, Witham, Essex, CM8 3YE.
Other Standard Analar Regents: Zinc Chloride, Silver Nitrate, Sodium Chloride, Ammonium Chloride Magnesium Perchlorate and conc. Acids. Copper Turnings.		BDA Chemicals Ltd., Bloom Road, Poole, Dorset, BH12 4NN.

Table 2.3

Dry box Instrumentation and Manufacturer's Specifications to be read in conjunction with figure 2.5.

A	Shaw Moisture Meter, Model SHA (Shaw Moisture Meters, Rawson Road, Westgate, Bradford, W. Yorks., BD1 3SQ.)
B	KNF Diaphargm Compressor Pump, Model No. 35.2E, pumping speed 55 dm^3min^{-1} with heads connected in parallel (KNF Neuberger UK Ltd., Ardington, Wantage, Oxon.)
C	Drallium Series 2000 Ball valves, type VR, (Drallium Fluid Components, Brett Drive, Bexhill-on-Sea, E. Sussex.)
D	Lintott Mk.1 Glovebox, refurbished and tested by Miller Howe Ltd., Watlington Industrial Estate, Watlington, Oxon.
E	Solenoid Valve, Series 27 (Black Automatic Controls, Leafield, Corsham, Wilts., SN13 9SP), operated via a series 80 pressure switch, type 8062 (address as above)

Table 2.4

CV data LiCl-KCl (64-36 m/o) melt at 430^{o}C [a]

(Ni/Ni(II) (10^{-2}m) reference electrode

Electrode reaction	E_p/V Melt
$2H_2O + 2e \rightarrow H_2 + 2OH^-$	-0.84
$2OH^- + 2e \rightarrow H_2 + 2O^{2-}$	-1.94
$2O^{2-} \rightarrow O_2 + 4e$	+0.5

[a] reference 17.

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Chapter 3

Binary Gaseous Diffusion Coefficients

3.1 Introduction

Binary diffusion coefficients of gases are important parameters needed in the design of reactors where chemical vapour transport or gas-phase reactions are involved[1]. Diffusion coefficient measurements fall into two groups, those aimed at gaining greater understanding of the intermolecular forces[2] and those, as in this work, aimed at obtaining data on systems of practical importance. In view of the scarcity of reliable experimental data for diffusion coefficients, they are commonly estimated from kinetic theory. Although experimental measurements are preferred, their determination is often time-consuming especially over a wide range of temperatures and pressures[3,4,5]. However the modified entrainment method provides a rapid and accurate technique for the measurement of binary gaseous diffusion coefficients at atmospheric pressure[6]. A reliable equation (3.3.1) orginally developed from binary pairs of spherical non-polar molecules at low pressure proposed by Chapman and Enskog using rigourous kinetic theory was extensively investigated by Hirschfelder, Bird and Sprotz[7]. This equation is used throughout this thesis to compare experimental data with theory or to derive accurate theoretical diffusivities in their absence.

In the present work, the modified entrainment method (MEM) was used to determine experimental values for the diffusivities of metal vapours (zinc and mercury) in non-reacting atmospheres (hydrogen, helium, nitrogen and argon). The work on the zinc-hydrogen system was also undertaken for the purpose of validating a newly-modified MEM rig (new purification and gas flow control systems) and a new design capsule (the re-entrant capillary pattern - see figure 2.2).

3.2 Binary Diffusion Coefficients - theory

The flow of material from one region to another is an example of mass transport. When a gas is of uniform density but non-uniform composition, the molecules diffuse through the system until the composition is uniform throughout. This molecular flux motion is the rate of flow passing through unit area in unit time commonly expressed in terms of mol $m^{-2}s^{-1}$ or kg $m^{-2}s^{-1}$. Experimental observation on the rate of diffusion or mass transport in one dimension (the Z direction) shows that the flux (J_i) is proportional to the concentration gradient

$$J_i \quad \alpha \quad -\frac{dN_i}{dZ} \qquad (3.2.1)$$

where N = nos. of molecules per unit volume (or mass) of species i. Mass flow occurs down a concentration gradient, as conventionally indicated by the negative sign and the constant of proportionality in the mass flux expression is D, the diffusion coefficient or diffusivity (see figure 3.1 - concentration decreasing to the right).

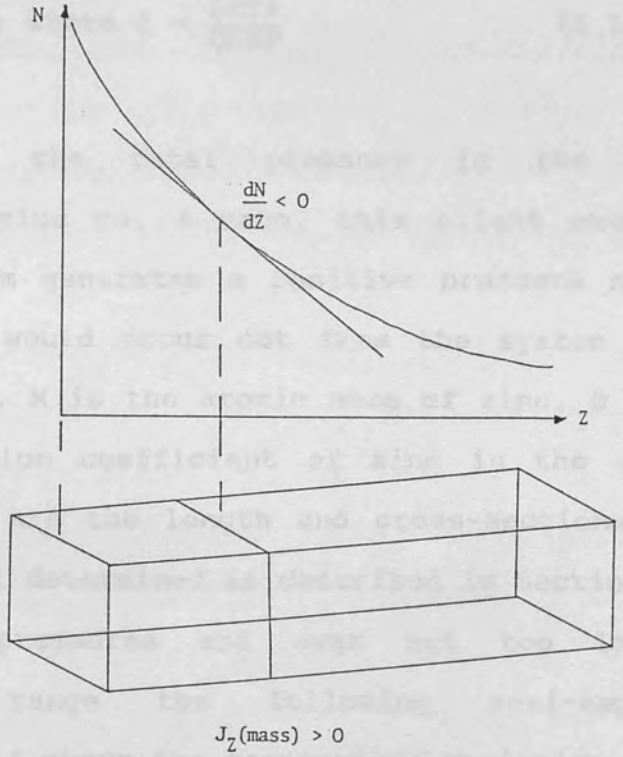

Figure 3.1 The Flux of Particles Down a Concentration Gradient

This is Fick's First Law,

$$J_i = - D_i\left[\frac{dN_i}{dZ}\right] \qquad (3.2.2)$$

The proportionality constant for a binary gaseous diffusion coefficient (D_{AB}) describes the relative molecular interaction (movement) between two different molecules (species A and species B) in a gas mixture.

For the sublimation of a single substance (say, zinc) during modified entrainment, the rate of weight loss ($\mathring{\omega}$) at temperature (T) is related to the equilibrium vapour pressure (p^{o}_{Zn}) by

$$p^{o}_{Zn} = P(1-e^{-\xi}) \text{ where } \xi = \frac{\mathring{\omega}RT\ell}{DAMP} \qquad (3.2.3)$$

where P is the total pressure in the system (atmospheric plus ca. 4 mmHg, this slight excess in the MEM system generates a positive pressure so that any leakages would occur out from the system rather than inwards), M is the atomic mass of zinc, D is the binary diffusion coefficient of zinc in the carrier gas, ℓ and A are the length and cross-sectional area of the channel determined as described in Section 1.4.

At low pressures and over not too large a temperature range the following semi-empirical relationship[4,8] shows the temperature variation of D_{AB}

$$D_{AB} = D_{O}\left[\frac{T}{T_{O}}\right]^{1+s} \qquad (3.2.4)$$

where $D_{O}/m^{2}s^{-1}$ = binary diffusion constant at reference temperature,

T_{O}/K = reference temperature, taken as 273.15 K.

For a simple molecular model of ideal rigid spheres, 1 + s = 1.5 independent of temperature. Actual gas pairs, however, have appreciably greater values of 1 + s, usually between 1.5 and 2. The inverse pressure dependence of the diffusion coefficient could also have been included, but the small fluctuation in atmospheric pressure during the course of the MEM experiments cause changes in D_{AB} that are within the random scatter of the results.

3.3 Estimation of Binary Gaseous Diffusion Coefficients

Chapman-Enskog, First-Order Approximation

The classical theory of the transport properties of dilute gases based on the Chapman-Enskog (C-E) solution of the Boltzmann equation has been fully described[7,9]. In the kinetic theory of a dilute binary gas mixture at low to moderate pressures Chapman and Enskog showed independently the working equation to be

$$D_{AB} = \frac{3}{16}\left[2\pi kT\,\frac{M_A+M_B}{M_A M_B}\right]^{\frac{1}{2}} \frac{1}{n\pi\sigma^2_{AB}\Omega_D}\, f_D \qquad (3.3.1)$$

where, M_A, M_B = molecular masses

n = number density of A + B

k = Boltzmann's constant

T = absolute temperature.

Ω_D, the collision integral for diffusion, is a function of temperature and depends upon the choice of the intermolecular force law between colliding molecules. σ_{AB} is a characteristic length. Finally, f_D is a correction term which is of the order unity. If $M_A \simeq M_B$, $1.0 \leqslant f_D \leqslant 1.02$ regardless of composition of the nature of the intermolecular forces. Only if the molecular masses are very unequal and the light component is present in trace amounts, is the value of f_D significantly different from unity, and even in such cases, f_D is usually between 1.0 and 1.1 [4].

When f_D is chosen as unity and n expressed by the ideal-gas law, equation (3.3.1) may be written as

$$\mathcal{D}_{AB} = 1.858 \times 10^{-7} T^{3/2} \frac{[(M_A+M_B)/M_A M_B]^{\frac{1}{2}}}{P\sigma_{AB}^{2}\Omega_D} \quad (3.3.2)$$

where

$\mathcal{D}_{AB}/\mathrm{m^2 s^{-1}}$ = binary diffusion coefficient for A in B

T/K = absolute temperature

P/atm = total pressure

$\sigma_{AB}/\text{Å}$ = collision diameter, distance centers of molecules at zero potential energy, i.e., separation between molecular centers of unlike pairs upon collision.

Ω_D = diffusion collision integral, dimensionless.

The collision integral has been tabulated as a function of kT/ϵ_{AB} where ϵ_{AB} is the minimum energy in the intermolecular force law between species A and B[7,10]. However in this work the analytical relations of Neufeld et al.[11] or Chen[12] which allows direct calculation of Ω_D with an accuracy comparable to that of the best tabulated data[10] have been used in equation (3.3.2).

Neufeld et al. equation is

$$\Omega_D = \frac{A}{T^{*B}} + \frac{C}{\exp DT^*} + \frac{E}{\exp FT^*} + \frac{G}{\exp HT^*} \qquad (3.3.3)$$

where $T^* = kT/\epsilon_{AB}$ $\quad A = 1.06036$ $\quad B = 0.15610$

$C = 0.19300$ $\quad D = 0.47635$ $\quad E = 1.03587$

$F = 1.52996$ $\quad G = 1.7674$ $\quad H = 3.89411$

and Chen's corresponding equation is

$$\Omega_D = A\left[\frac{kT}{\epsilon_{AB}}\right]^{-B} + 2\left[\frac{10kT}{\epsilon_{AB}}\right]^{-C}$$

where $A = 1.075$

$B = 0.1615$

$$C = 0.74\log_{10}\left[\frac{10kT}{\epsilon_{AB}}\right] \qquad (3.3.4)$$

These equations have been calculated assuming the intermolecular potential is the Lennard-Jones (12-6) potential, consequently ϵ_{AB} and σ_{AB} are the characteristic (12-6) LJ parameters.

Lennard-Jones and Devonshire (see ref. 7) proposed an equation for the intermolecular energy (Φ) between two molecules at a distance of separation r as

$$\Phi_{(r)} = 4\epsilon\left[\left[\frac{\sigma}{r}\right]^{12} - \left[\frac{\sigma}{r}\right]^{6}\right] \qquad (3.3.5)$$

and illustrated in figure 3.2.

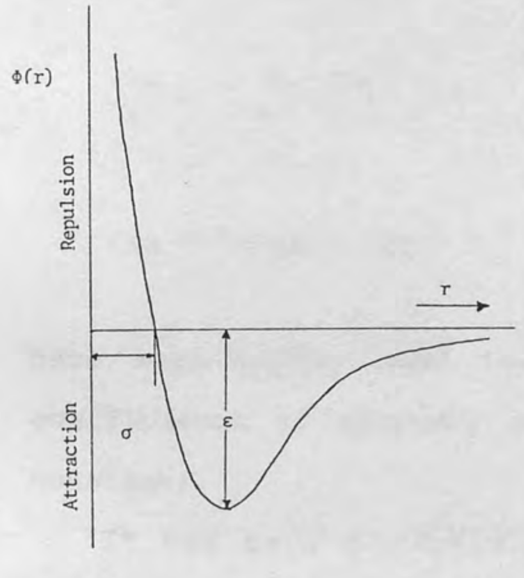

Figure 3.2 Lennard-Jones (12-6) Potential

This potential has been widely used in statistical mechanical calculations of low density gas phenomena. The LJ (12-6) potential continues to be employed in much thermophysical and thermodynamic research as a convenient and realistic characterisation.

Further, more elaborate potentials are only partially successful in their interpretation of the results for complicated molecules. Application of Chapman-Enskog theory to the viscosity of pure gases and the corresponding state correlations has led to the formation of many useful values of ϵ and σ[13].

Most experimental data have been obtained for pure gases, so that potential parameters are available only for the interaction of like molecules. In principle, the potential parameters for the interactions of unlike molecules can be derived from the transport properties of mixtures, but the inversion of such data is a formidable theoretical problem. In the case of LJ (12-6) potential, the semi-empirical combination rules (Lorentz-Berthalot rules)

$$\frac{\epsilon_{AB}}{k} = \left[\frac{\epsilon_{AA}}{k}\,\frac{\epsilon_{BB}}{k}\right]^{\frac{1}{2}} \qquad (3.3.6)$$

$$\sigma_{AB} = \tfrac{1}{2}(\sigma_{AA} + \sigma_{BB}) \qquad (3.3.7)$$

have been widely used for predicting the diffusion coefficients of mixtures of gases[14] (k = Boltzmann's constant).

It has been demonstrated that ϵ-σ parameter sets determined from second virial coefficients, viscosity or diffusion coefficients can differ slightly in magnitude. The form of the Lennard-Jones potential is such that when regressing experimental data to find "best" values of ϵ/k and σ, one cannot separate these potential parameters. That is ϵ/k and σ are strongly interdependent and a high value of σ with low value of ϵ/k will reproduce transport properties with the same precision as from a low value of σ and a high ϵ/k.

Using (ϵ/k,σ) pairs (or sets) from the same source i.e. both from second virial coefficients or both from viscosity data then diffusion coefficients may be estimated to about ± 7% for non-polar mixtures and to about ± 12% for mixtures of polar gases.

Diffusion coefficients are relatively insensitive to the choice of ϵ and in the absence of experimental or recommended data, they were estimated from Svehla's linear correlation[15] of ϵ and T_b (normal boiling point)

$$\frac{\epsilon}{k} = 1.18T_b \qquad (3.3.8)$$

A method for estimating σ of monatomic and diatomic using the mean radius of an electron in the outermost electronic orbital has been proposed[15,16]. By assuming that two colliding molecules begin to repel when their change distributions, begin to overlap, the following equation was obtained.

$$\sigma_{monatomic} = 2r + 1.8 \qquad (3.3.9)$$

where r is the mean radius of the outermost electronic orbital (see ref. 15 and 16) and 1.8 is an empirical constant adjusted to agree with experimentally determined values of σ. Similar empirical relationships can be derived to diatomic and triatomic molecules[15,16].

Intuitively σ may be expected to correlate with some other parameter which quantifies the "size" of a molecule, e.g. $\sqrt[3]{\text{circumscribed sphere}}$, $\sqrt[3]{\text{molar volume}}$ etc., the criteron for the chosen function is that it must be readily available or easily calculated. The list in Appendix C of ref. 3, tabulates Lennard-Jones constants for 76 species including 18 diatomic or linear polyatomics. Rejecting data for I_2 and HI, the LJ force constants for the remaining 16 species gave a satisfactory linear correlation (r^2 - 0.91) with the square root of the moment of inertia, I/g cm^2

$$\sigma/\text{Å} = 3.411\pm0.087 + (0.549\pm0.047)10^{19}\sqrt{I} \qquad (3.3.10)$$

and this correlation was used to determine σ_{ZnCl_2}= 4.64Å and $\sigma_{Zn_2Cl_4}$ = 5.24Å. For Zn_2Cl_4, D_{2h} symmetry was assumed, the internal bond angles set to 90°, and the bridging bond lengths set to 1.1 times the terminal bond lengths which were assumed to be 2.05Å as in $ZnCl_2$. Finally $I(Zn_2Cl_4) = (I_xI_yI_z)^{1/3}$ where I_i are the principal moments. These structural assumptions are common to all M_2Cl_4 species quoted in JANAF tables[17]. Chapman and Enskog have shown that for binary diffusion there is only a very small compositional dependence and this is only significant when $M_A >> M_B$. Consequently no account of this was taken in the experiment work to determine D_{AB}. The situation is quite different when systems of three or more gases were investigated, that composition dependence was taken into account by applying a multicomponent diffusion correction procedure (discussed in section 3.4).

Finally in the case of polyatomic gas mixtures, it has been demonstrated[18] that, owing to the insensitivity or robustness of the diffusion coefficient (and viscosity) to inelastic collisions and to the asymmetry of the potential, equation (3.3.2) still retains its validity.

Graham's Law of Scaling

Another technique used to estimate binary gaseous diffusion coefficents is by using Graham's Law of Scaling. The diffusion coefficients of gases 2 and 3 into a reference gas 1 should vary inversely as the square root of the molecular weights of 2 and 3

$$\frac{D_{13}}{D_{12}} = \left[\frac{M_2}{M_3}\right]^{\frac{1}{2}} \qquad (3.3.11)$$

It has been stressed[19] that the above equation is actually a crude approximation for most systems, although it is correct in the limiting case that the reference gas 1 has molecules which are infinitely large and heavy compared to the molecules of 2 and 3. A more rigorous scaling expression is

$$\frac{D_{13}}{D_{12}} = \left[\frac{M_2}{M_3}\right]^{\frac{1}{2}} \left[\left[\frac{M_1+M_3}{M_1+M_2}\right]^{\frac{1}{2}} \frac{\sigma^2_{12}\Omega_{12}}{\sigma^2_{13}\Omega_{13}}\right] \qquad (3.3.12)$$

This equation (3.3.12) was used to scale the results for zinc chloride from a system with structural similarity for which reliable experimental data exist. The chosen reference system was CO_2-Ar for which[3]

$$D(CO_2,Ar)/m^2s^{-1} = 1.74 \times 10^{-9}T^{1.646}/\exp(89.1/T)$$

$$(296\text{-}1800\ K) \qquad (3.3.13)$$

Applying the usual combining rules for σ_{12} and ϵ_{12} calculated via the equations (3.3.6 to 3.3.8), correlating with the square root of moment of inertia shown previously in this section and interpolating Ω_D using the appropriate formula[12], diffusion coefficient equations for zinc chloride monomer and dimer were estimated from equation (3.3.12) over the temperature range 630 to 980 K then linearly regressed to a power formula in T

$$D(ZnCl_2,Ar)/m^2s^{-1} = 8.624 \times 10^{-6}(T/273.15)^{1.760} \qquad (3.3.14)$$

$$D(Zn_2Cl_4,Ar)/m^2s^{-1} = 6.793 \times 10^{-6}(T/273.15)^{1.761} \qquad (3.3.15)$$

3.4 Multicomponent Diffusion with One Majority Component

In complex equilibria, the effect of multicomponent diffusion (the influence of a third gas on the diffusion flux of the first into the second) has been theoretically worked out[20]. The algebra is tedious, particularly for more than three components.

For modified entrainment systems studied two points are relevant

1) they are dilute gas mixtures in the presence of a majority component, for example, the minority components $ZnCl_2(g)$, $Zn_2Cl_4(g)$ and $Zn(g)$ in excess argon or hydrogen acting as the bulk carrier gas. The kinetic theory of multicomponent mixtures of dilute gases via Stefan-Maxwell equations[21] show that in order to compute the coefficients of such mixtures all that is necessary is information about the binary diffusion coefficient for each pair of constituents.

2) systems where the majority component in H_2 must be treated with caution - here multicomponent diffusion effects are often quite significant, qualitatively because the intermolecular intersection of H_2 is unusual when its small size is compared with the inorganic species present. The experimental temperatures in this work were too high for quantum effects with H_2 to be significant.

Equation and Format used for Multicomponent Diffusion (MCD) in Modified Entrainment Systems

Using a second-order approximation for multicomponent diffusion[20], it has been shown that the diffusion coefficient D(HCl,m) (where m = mixture of the species in the gas phase) may be replaced by the binary coefficient *D*(HCl,m) (where now m = the majority component, taken for the example to be Ar subsequently) divided by a composition dependent factor γ_{HCl}:

$$D_{HCl} = \mathit{D}_{HCl}/\gamma_{HCl} \qquad (3.4.1)$$

where

$$\gamma_{HCl} = 1 + a_{HCl}\epsilon + b\xi_{HCl}$$

and

$$\epsilon = \frac{p^{o}_{HCl}}{(p^{o}_{HCl}+p^{o}_{Ar})}$$

and a and b are functions of other binary diffusion coefficients and fluxes (see below). However at low values of ϵ the gas mixture is sufficiently dilute so that the gamma factor is close to unity. The flow of the transporting and carrier gases are controlled by mass flow controllers calibrated in $cm^3\ min^{-1}$ (stp).

Hence the pressure fraction (ϵ, overleaf) may be re-written in terms of flow rates (FR)

$$\epsilon = \frac{FR(HCl)}{FR(Ar) + FR(HCl)}$$

Notice that $\epsilon = 0$ except when HCl(g) is used as a reactive gas (chemical vapour transport process), mixed with argon or hydrogen as carrier gas.

The exact form of the coefficients a and b in (3.4.1) is not derived in detail in this thesis. However, the single most important aspect of the derivation[20] is that the flux of any species may be written as a first order linear differential equation, the solution of which is the concentration of that species as a function of distance along the channel. To solve these equations, the concentration (mole fraction, x_i) is written as a power series in ϵ, truncating at order two

$$x_i = f_1\epsilon + f_2\epsilon^2 \qquad (3.4.2)$$

This is the origin of the description, "a second order approximation".

Example of MCD correction for Zinc Sulphide Transport in mixture of HCl(g) and Ar(g)

The relevant equilibria are (consult Chapter 5, Appendix A2.4 and A3.5 for further details)

$$
\begin{array}{rcll}
ZnS(c) + 2HCl(g) & = & ZnCl_2(g) + H_2S(g) & K_{12} \\
2ZnCl_2(g) & = & Zn_2Cl_4 & K_2 \\
ZnS(c) & = & Zn(g) + \tfrac{1}{2}S_2(g) & K_{10} \\
H_2(g) + \tfrac{1}{2}S_2(g) & = & H_2S(g) & K_{11}
\end{array}
$$

The flow rates of HCl and Ar were 6.0 and 84.0 $cm^3 min^{-1}$ (stp) respectively giving $\epsilon = 0.0667$. The coding for the participating gaseous species used for the written computer program (ZNSHCl10.FOR) in Appendix 3.5 was

$ZnCl_2$	1	Zn	5
Zn_2Cl_4	2	S_2	9
HCl	3	H_2S	10
H_2	4	Ar	11

then,

1, 2, 4, 5, 9, 10 are MINORITY species j,

3 is the transporting species h,

11 is the MAJORITY species A.

Gamma correction for minority species

$$\gamma_i = 1 + a_i\epsilon + b\xi_i \qquad (3.4.3)$$

where

$$a_i = \left[\frac{D_{iA}}{D_{ih}} - 1\right]$$

$$b_i = \left\{\sum_j \left[\frac{1}{2}\left(\frac{D_{iA}}{D_{ij}} - 1\right]\left(\frac{D_{iA}}{D_{jA}} - 1\right]\frac{J_i}{J}\right] - \frac{1}{2}\right\}$$

The relationship between i and j is summarised in the following matrix,

i	j					
1	2	4	5	9	10	3
2	1	4	5	9	10	3
4	1	2	4	9	10	3
5	1	2	4	9	10	3
9	1	2	4	5	10	3
10	1	2	4	5	9	3

For the transporting species (HCl or 3), the coefficient b_i is similarly defined but a_i is defined differently

$$\gamma_3 = 1 + a_3\epsilon + b_3\xi_3$$

where

$$a_3 = -\left[\frac{D_{3,11}}{D_{3,1}} - 1\right]\frac{J_1}{J} - \left[\frac{D_{3,11}}{D_{3,2}} - 1\right]\frac{J_2}{J} \qquad (3.4.4)$$

$$- \left[\frac{D_{3,11}}{D_{3,4}} - 1\right]\frac{J_4}{J} - \left[\frac{D_{3,11}}{D_{3,5}} - 1\right]\frac{J_5}{J}$$

$$- \left[\frac{D_{3,11}}{D_{3,9}} - 1\right]\frac{J_9}{J} - \left[\frac{D_{3,11}}{D_{3,10}}\right]\frac{J_{10}}{J} - \frac{J}{J_3}$$

b_3 is given by the equation above for b_i. i and j are related as before

i	j					
3	1	2	4	5	9	10

In all of the expressions for a_i and b_i the ratios of the binary diffusion coefficients are estimated from Graham's law scaling viz

$$D_{(i,j)} = \left[\frac{D_1}{D_j} - 1\right] \simeq \left[\frac{M_j}{M_i}\right]^{\frac{1}{2}} - 1 \qquad (3.4.5)$$

e.g.

$$D_{(11,4)} = \left[\frac{D_{A_{11}}}{D_{A_4}} - 1\right] \simeq \left[\frac{M_4}{M_{11}}\right]^{\frac{1}{2}} - 1$$

where M_j is the molecular weight for species j.

Figure 3.3 is a flowchart which outlines the computational method for calculating MCD gamma corrections (γ_i). The method employed is reiterative because the equation for γ_i (3.4.3) contains the transport function, ξ_i, which itself depends on $D_{(i,m)}$. Consequently the first estimate of $D_{(i,m)}$ is set to the corresponding binary $\mathcal{D}_{(i,m)}$. This is equivalent to setting γ_i to unity. Iteration is initiated, successively updating $D_{(i,m)}$, until consecutive values of γ_i differ by < 1 in 10^4 (the termination criteron). Binary gaseous diffusion coefficients are determined from experimental results or estimated by the Chapman-Enskog first order approximation (see section 3.5). It was found that the γ_i corrections were always close to unity

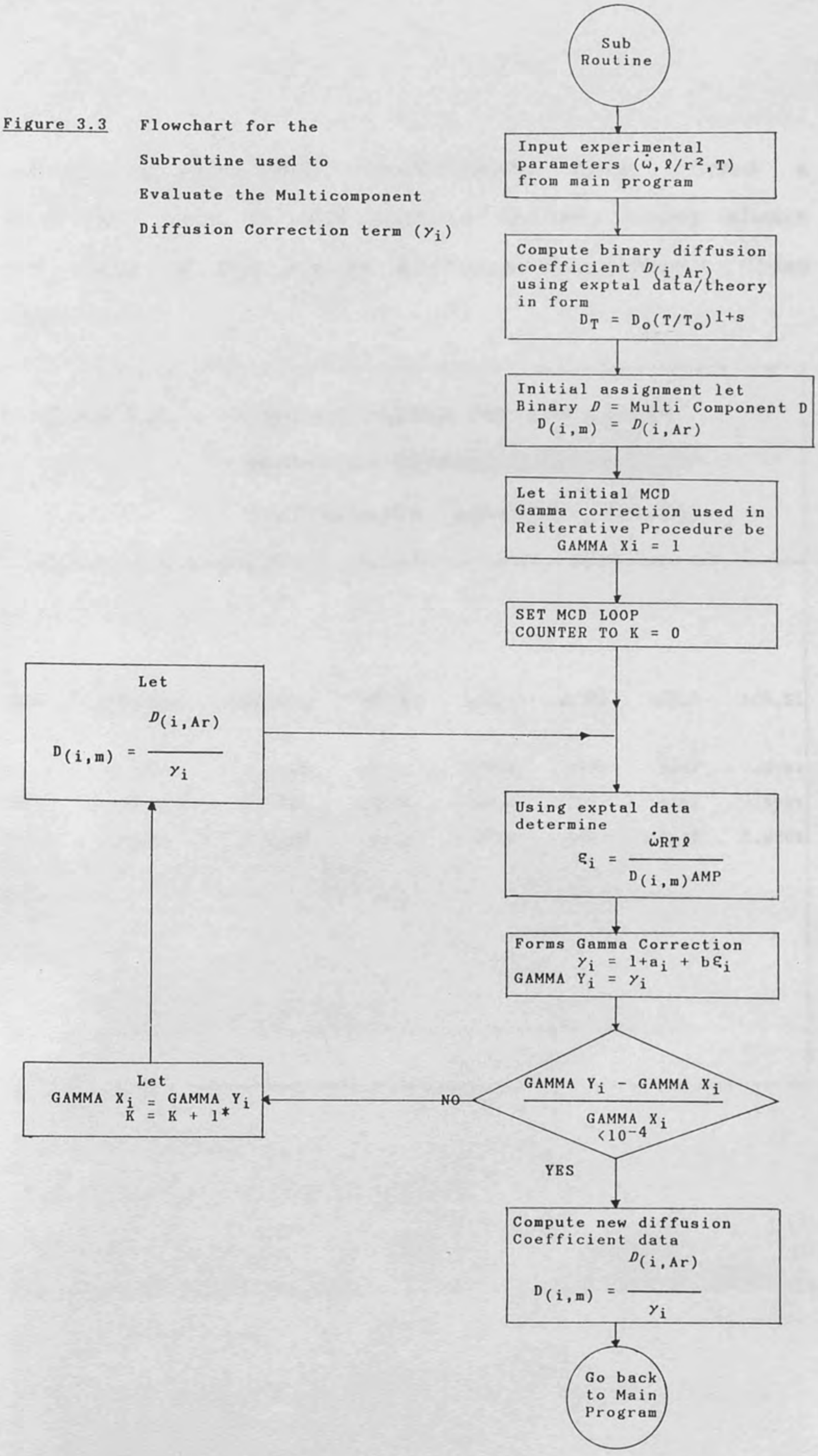

Figure 3.3 Flowchart for the Subroutine used to Evaluate the Multicomponent Diffusion Correction term (γ_i)

* typically K $\leqslant$ 3

indicating the MCD coefficients only played a secondary role in MEM systems chosen, being always similarly to the binary diffusion coefficients (see table 3.1)

Table 3.1 Typical values for the multi-component diffusion correction coefficients (equation [3.4.3])

T/K	$\gamma[ZnCl_2]$	$\gamma[Zn_2Cl_4]$	$\gamma[HCl]$	$\gamma[H_2]$	$\gamma[Zn]$	$\gamma[S_2]$	$\gamma[H_2S]$
1024	0.9974	0.9969	.9124	.9989	.9978	.9987	.9983
1159	0.9975	0.9965	.9525	1.0010	.9985	.9993	.9997
1252	0.9977	0.9959	.9681	1.0028	.9991	1.0002	1.0009

3.5 Binary Gaseous Diffusion Coefficients of Zinc and Mercury in Inert Gases

The transport of Zn(g) in H_2 is a suitable process for the validation of the vapour transport equipment. Also the result is required for the analysis of the ZnS/H_2 transport experiments in Chapter 5. The equations relating the experimental rate of mass loss ($\mathring{\omega}$), the temperature (T), the channel resistance (ℓ/r^2) and the equilibrium vapour pressure of zinc (p^o_{Zn}) were given in detail in chapter 1.4 as

$$p^o_{Zn} = P(1-e^{-\xi}) \text{ where } \xi = \frac{\mathring{\omega}RT\ell}{D_{(Zn,H_2)}AMP} \qquad (3.5.1)$$

$$\therefore D_{(Zn,H_2)} = \frac{\mathring{\omega}RT\ell}{[AMP\ln(1 + p^o_{Zn}/P)]}$$

The transport of Zn(g) in H_2 was studied in the range 689-1118 K (T_m = 693 K; T_b = 1186 K). Fifty-six points were recorded with approximately 1 mg mass loss per point; the corresponding rates of mass loss ($\mathring{\omega}$) range from 3.22×10^{-12} kg s^{-1} at 693 K to 1.64×10^{-8} kg s^{-1} at 1118 K. The MEM data on zinc and mercury are collected in Appendix A4.1 and A4.2.

The equilibrium vapour pressure of molten zinc (p^o_{Zn} in equation (3.5.2)) was taken from a critical compilation by Nezmeyanov[22]

$$\log_{10}(p^{o}_{Zn}/Pa) = A + B/T + CT + D\log_{10}T \qquad (3.5.3)$$

where $A = -5.7941$

$B = -5330.735$

$C = -0.00161644$

$D = 5.59972$

over assumed T_m (693 K) to T_b (1186 K) temperature range.

A more recent compilation of thermodynamic data for the elements[23] includes no further reliable results over the temperature range of interest, although the recommended values for the vapour pressure of liquid zinc are 5% greater than those calculated using the above equation. The temperature dependence of gas-phase binary diffusion coefficients was expressed in the usual form (see section 3.2) to give

$$D_{(Zn,H_2)} = 81.086 \times 10^{-6}\ (T/273.15)^{1.539} \qquad (3.5.4)$$

temperature range between 693 to 1118 K.

Rejection of 1 rogue datum point improved the correlation coefficient (r^2) for the regression of $\ln D_{(Zn,H_2)}$ vs. $\ln(T/273.15)$ from 0.967 to 0.990. The diffusion coefficient constants and subsequent data are compared with literature and theoretical data in tables 3.2 to 3.4 and figure 3.4

Table 3.2 Comparison of Binary Diffusivities of $Zn(g)$ in H_2, $T_O = 273.15$ K

Temp. Range/K	$10^6 D_O/m_2 s^{-1}$	(1+s)	Source
724 - 1027	68.6	1.709	Ref. 6 [a]
720 - 1120	71.4	1.761	Theory [b]
- - -	77.0	1.50	Hard Sphere[c]
693 - 1118	81.1	1.539	This work

[a] previous result obtained in this laboratory

[b] Chapman-Enskog theory (see section 3.3)

[c] E.A. Moelwyn-Hughes, "Physical Chemistry", 2nd edition, 1965, pp 59-62, Pergamon.

Table 3.3 Binary Diffusivities of $Zn(g)$ in H_2 700-1100 K $10^6\ D_{AB}/m^2 s^{-1}$

T/K	Ref. 6 [a]	Theory	Hard Spheres	This Work [b]
700	3.43	3.74	3.16	3.45
900	5.26	5.83	4.61	5.08
1100	7.42	8.30	6.22	6.92

[a] Integral capsule [b] Re-entrant capsule

Table 3.4 Lennard-Jones Parameters used to Calculate D_{AB} from C-E Theory

Substance	σ/Å	ϵ/k_BK
Zn	2.284	1393
Hg	2.969	750
H_2	2.827	59.7
He	2.608	10.22
N_2	3.798	71.4
Ar	3.408	119.9

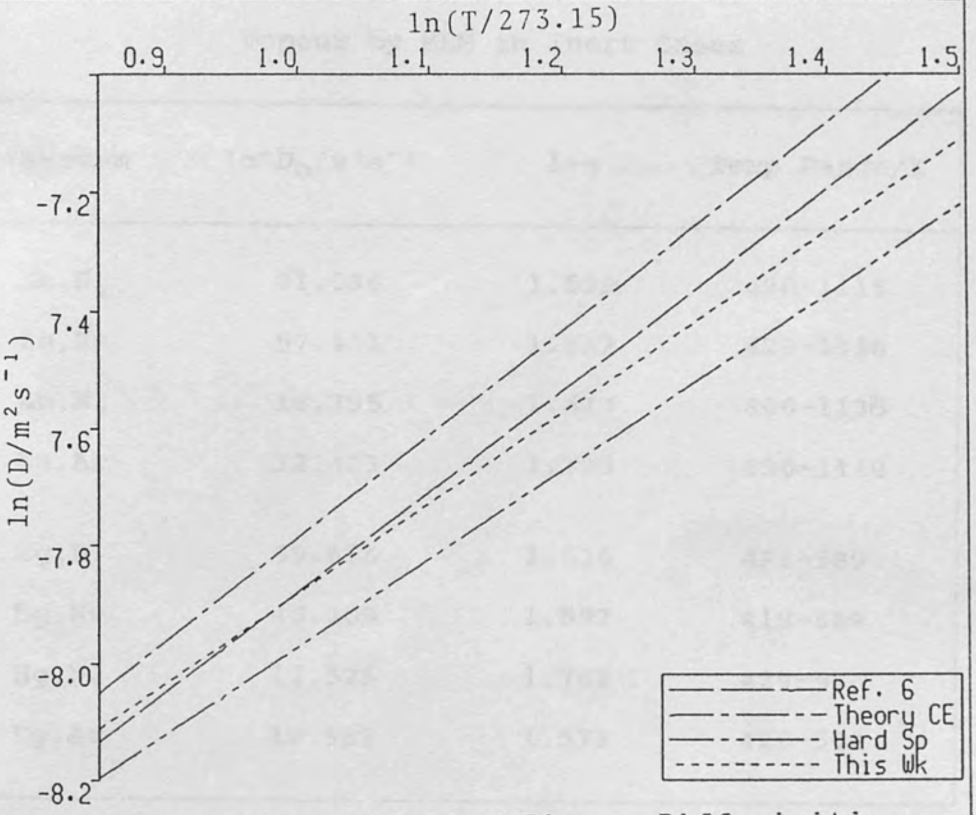

Figure 3.4 Comparison of Binary Diffusivities of Zinc(g) in Hydrogen 650-1200 K

Values of D_O and (1 + s) shown in table 3.2 are all different but the corresponding value of D_T agrees to within 74% over the complete temperature range. Ignoring the Hard Sphere result (an admittedly crude model) the agreement is better than 84%. The form of these constants D_O & 1 + s are analogous to LJ constants ϵ & σ is such that when calculating diffusion coefficients one cannot be used without the other. A corresponding study of the transport of Zn(g) in helium, nitrogen and argon yielded the results in table 3.5. Similar results for Hg(g) in these gases are also collected in table 3.5.

Table 3.5 Diffusion Coefficient Studies of Metal Vapour by MEM in Inert Gases

System	$10^6 D_O/\mathrm{m^2 s^{-1}}$	1+s	Temp.Range/K
Zn,H_2	81.086	1.539	690-1118
Zn,He	57.431	1.632	829-1118
Zn,N_2	18.795	1.673	800-1135
Zn,Ar	12.423	1.793	820-1140
Hg,H_2	59.616	1.535	421-589
Hg,He	46.409	1.597	419-589
Hg,N_2	12.525	1.761	429-590
Hg,Ar	10.988	1.573	429-590

The equation for the equilibrium vapour pressure of liquid mercury was that quoted in a recent critical re-determined by Ambrose and Sprake[24] who used

$$\log_{10}(p_{Hg}/\mathrm{kPa}) = A + B/T + CT + DT^2 \qquad (3.5.5)$$

Temp. Range 400-688 K

$A = 7.658\ 791$

$B = -3279.230$

$C = -9.680\ 031 \times 10^{-4}$

$D = 4.115\ 463 \times 10^{-7}$

An earlier critical compilation by Nesmeyanov[22] makes no significant differences to the calculated diffusion coefficient.

Values of $\ln(D_{273.15})$ and (1+s) generally a non integral exponent (characteristic for a particular pair) are given in table 3.6, together with their standard deviation of "coefficients" regress from the fitted line of $\ln D_T$ vs. $\ln(T/273.15)$. These results are also compared graphically in figures 3.5 and 3.6. Notice the temperature dependence of the diffusion coefficient for each system was well reproduced by fitting the experimental data to the logartithmic form of equation (3.5.4)

$$\ln(D_{AB}/\mathrm{m^2s^{-1}})_T = \ln(D_{273.15}) + (1+s)\ln(T/273.15) \qquad (3.5.5)$$

The plots are linear implying gas ideality behaviour in the MEM systems studied.

Table 3.6 Diffusivities of Zinc [690-1140 K] and Mercury [421-590 K] all at 1 Atm.

System	$\ln D_o$	1 + s	r^2 [a]	Pts.[b] used
Zn,H_2	-9.4200±0.0264	1.5391±0.0209	0.990	55/56
Zn,He	-9.7649±0.0148	1.6318±0.0116	0.998	44/49
Zn,N_2	-10.8819±0.0481	1.6733±0.0380	0.964	74/75
Zn,Ar	-11.2959±0.0754	1.7934±0.0575	0.960	43/50
Hg,H_2	-9.7276±0.0136	1.5349±0.0217	0.989	57/62
Hg,He	-9.9674±0.0235	1.5785±0.0372	0.974	50/53
Hg,N_2	-11.2878±0.0181	1.7613±0.0287	0.988	48/53
Hg,Ar	-11.4187±0.0194	1.5731±0.0287	0.986	46/50

[a] r^2 = correlation coefficient

[b] Pts used =

$$\frac{\text{total no. of Pts. collected - no. of pts rejected}}{\text{total no. of pts collected}}$$

$$\ln D_T = \ln D_O + (1+s)\ln(T/T_O)$$

$$D_T = D_O(T/T_O)^{1+s}$$

where o = 273.15 K reference temp.

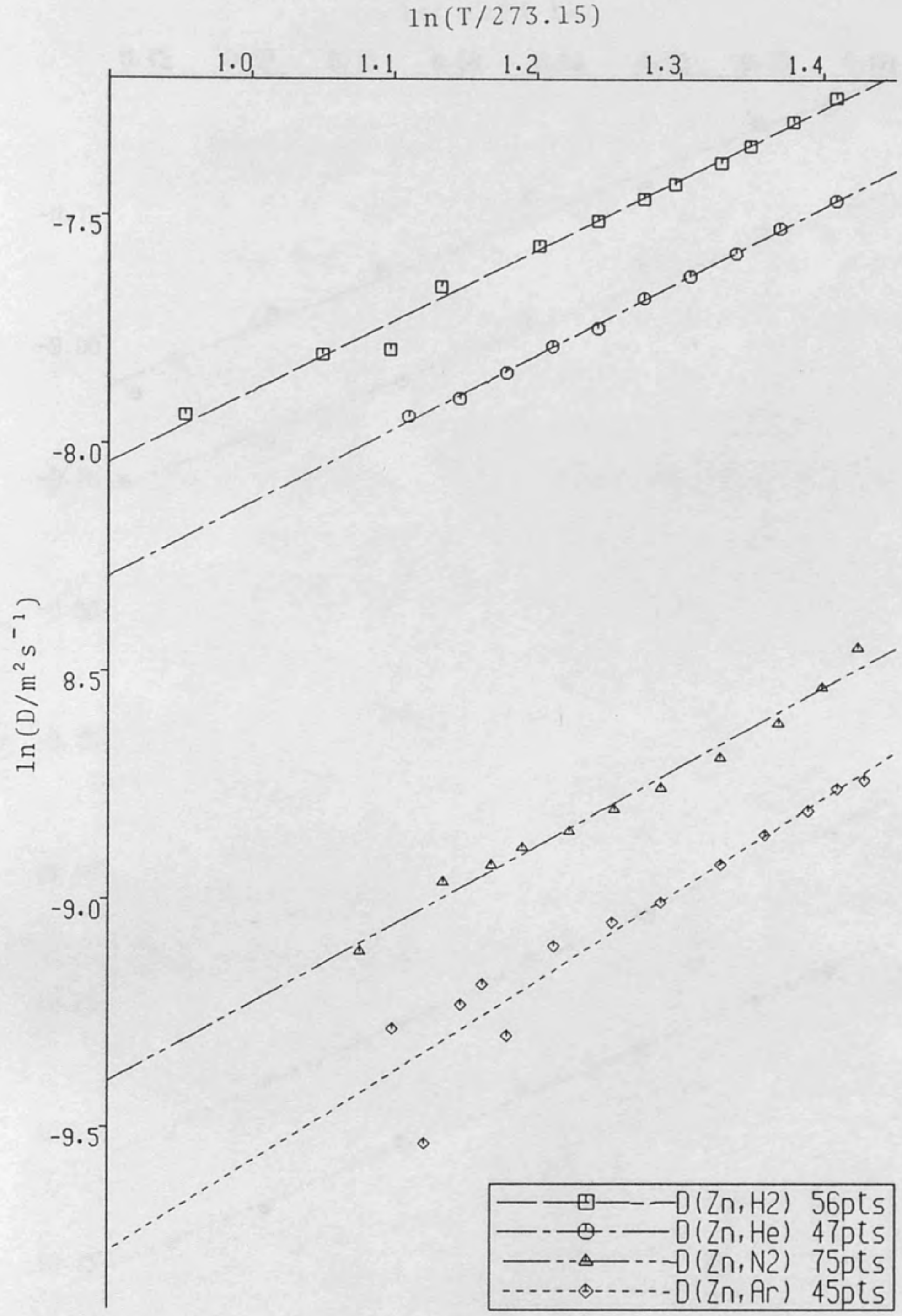

Figure 3.5 Binary Gaseous Diffusion Coefficients of Zinc in Inert Gases 690-1140 K

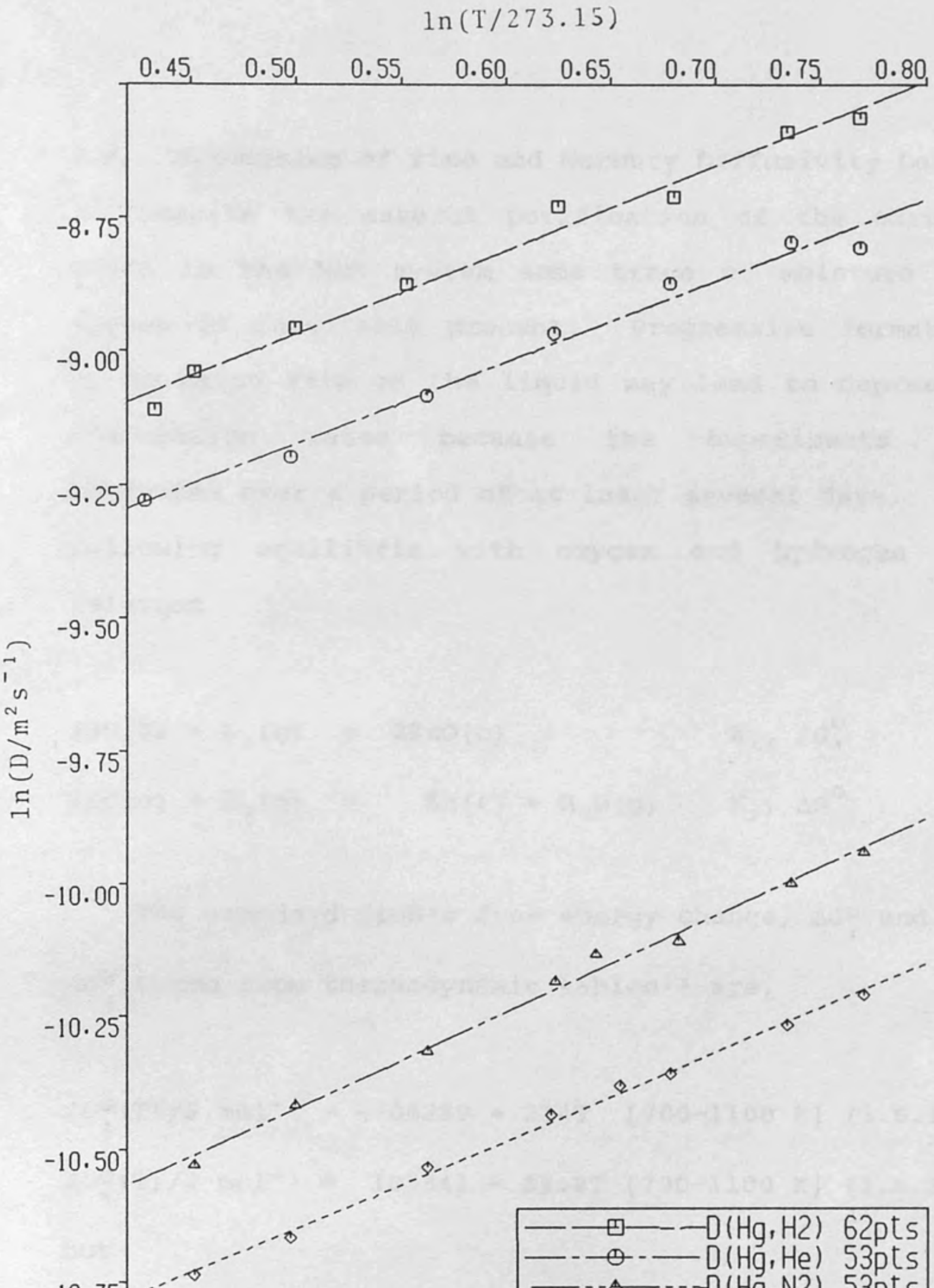

Figure 3.6 Binary Gaseous Diffusion Coefficients of Mercury in Inert Gases 420-600 K

3.6 Discussion of Zinc and Mercury Diffusivity Data

Despite the careful purification of the carrier gases in the MEM system some trace of moisture and oxygen is inevitably present. Progressive formation of an oxide film on the liquid may lead to depressed evaporation rates because the experiments are conducted over a period of at least several days. The following equilibria with oxygen and hydrogen are relevant

$$2Zn(\ell) + O_2(g) = 2ZnO(c) \qquad K_1,\ \Delta G^o_1$$

$$ZnO(c) + H_2(g) = Zn(\ell) + H_2O(g) \qquad K_2,\ \Delta G^o_2$$

The standard Gibb's free energy change, ΔG^o_1 and ΔG^o_2 taken from thermodynamic tables[25] are,

$$\Delta G^o_1(T)/J\ mol^{-1} = -706289 + 214T \quad [700\text{-}1100\ K] \quad (3.6.1)$$

$$\Delta G^o_2(T)/J\ mol^{-1} = 105541 - 52.8T \quad [700\text{-}1100\ K] \quad (3.6.2)$$

but

$$\Delta G_T/J\ mol^{-1} = \Delta G^o_i(T) + RT\ln Z_i \qquad (3.6.3)$$

where $i = 1$ or 2,

$$Z_1 = \frac{a^2_{ZnO}}{a^2_{Zn}p_{O_2}} \text{ for } K_1, \text{ and } Z_2 = \frac{a_{Zn}p_{H_2O}}{a_{ZnO}p_{H_2}} \text{ for } K_2$$

Thus the position of the equilibria may be assessed at any temperature given the oxygen and moisture content of the carrier gas stream. Postulating a pessimistic level of oxygen impurity to be 5 ppm(v) and water vapour to be 20 ppm(v) and assuming the relevant activities of the condensed phases to be equal to 1 then

$$\Delta G_1(T) = \Delta G_1^{O}(T) + 101.5T \qquad (3.6.4)$$

and

$$\Delta G_2(T) = \Delta G_2^{O}(T) - 90.0T \qquad (3.6.5)$$

Table 3.7 Thermodynamic values of ΔG_1 and ΔG_2 Over a temperature range 700-1100 K Assuming 5 ppm(v) O_2 and 20 ppm(v) H_2O impurities

T/K	ΔG_1/kJ mol^{-1}	ΔG_2/kJ mol^{-1}
700	-476	5
900	-410	-23
1100	-344	-51

From table 3.7, it shows that ΔG_1 is negative and this indicates the formation of an oxide layer on molten zinc is thermodynamically feasible. At regular intervals the sample was baked for a short period in hydrogen at 1173 K to remove any oxide film. A similar procedure was followed in the experiments with Hg, except that the baking temperature was much lower, 590 K.

Similarly, thermodynamic values[25] for mercury(II) oxide and its reduction by a hydrogen gas stream were explored.

$$2\mathrm{Hg}(\ell) + \mathrm{O_2(g)} \;=\; 2\mathrm{HgO(c)} \qquad K_3,\ \Delta G_3^{\circ}$$

$$\mathrm{HgO(c)} + \mathrm{H_2(g)} \;=\; \mathrm{Hg}(\ell) + \mathrm{H_2O(g)} \qquad K_4,\ \Delta G_4^{\circ}$$

The relevant thermodynamic relationships are given in eqs. (3.6.6) and (3.6.7) and table 3.8 assuming pessimistic values of impurities of oxygen and water.

O_2 content 5 ppm(v)

$$\Delta G_3(T)/\mathrm{J\ mol^{-1}} = \Delta G_3^{\circ}(T) + 101.5T \qquad (3.6.6)$$

where

$$\Delta G_3^{\circ}(T)/\mathrm{J\ mol^{-1}} = -185549 + 300T - 28.3T \qquad [248\text{-}600\ \mathrm{K}]$$

and

H_2O content 20 ppm(v)

$$\Delta G_4/\text{J mol}^{-1} = \Delta G_4^{O}(T) - 90.T \qquad (3.6.7)$$

where

$$\Delta G_4^{O}(T)/\text{J mol}^{-1} = -146822 - 170T + 36.3T\log_{10}T$$

[248-600 K]

Table 3.8 Thermodynamic Values of ΔG_3 and ΔG_4 Over a temperature range 298-600 K Assuming 5 ppm(v) O_2 and 20 ppm(v) H_2O impurities

T/K	ΔG_3/kJ mol^{-1}	ΔG_4/kJ mol^{-1}
298	-90	-20
400	-59	-21
600	+1	-24

As shown in tables 3.7 (ΔG_1) and 3.8 (ΔG_3) the assumption of ≃ 5 ppm of O_2 in the carrier gas stream, oxide formation is thermodynamically favourable in both experiments with Zn and Hg. Both HgO and ZnO are less dense than the liquid metals and consequently a thin film will slowly develop on the surface.

Ultimately this will constitute a kinetic barrier to evaporation and the rates of mass loss will become time-dependent and irreproducible. This was not observed and hence it must be concluded that the regular baking H_2 was sufficient to remove any oxide layer.

The existence of gaseous mercury cluster (mainly dimers) has been reported[26,27]. However, in our experimental temperature, their concentration is << 1% by extrapolation of the equation in ref. (27) and hence their presence was ignored.

3.7 Validation of MEM Rig

The MEM has been exploited to measure binary diffusion coefficients when the vapour pressure of the material is known and the carrier gas used is inert to the evaporated species. The $D_{(\mathrm{Zn,carrier\ gas})}$ results agree well with the previously determined values obtained in this laboratory using an older design "integral" channel instead of a "re-entrant" channel capsule. This agreement is regarded as a satisfactory test of the equipment and its associated hardware.

3.8 Binary Diffusion Coefficients: A Comparison with Experimental Results with Theoretical Predictions

Diffusion coefficients obtained from the experiments described above are compared with those calculated from the Chapman and Enskog first approximation theory for binary pairs of spherical non-polar molecules at low pressures and with literature work where appropriate in tables 3.2, 3.3, 3.9 and 3.10.

In general, the agreement between experimental and theoretical data is satisfactory and the extent of deviation is similar in both the zinc and the mercury (see tables 3.9 and 3.10), except in the case of the argon results. The rate of diffusion decreases as expected with increasing molecular mass of the carrier gas w.r.t. the metal used. Diffusion between metal vapour and hydrogen carrier gas is about 5 times faster than in the heaviest gas used, argon. Hence, when using hydrogen as a carrier gas in MEM the sample will be depleted about 5 times quicker than in argon, since the measured experimental parameter ($\mathring{\omega}$) is directly related to the diffusion coefficients.

Table 3.9 Diffusivities of Zinc in Inert Gases

$$\text{units} = \frac{D(\text{Zn,Carrier Gas}) \times 10^{-6}}{m^2s^{-1}}$$

	T/K	ref.1	expt.	C-E	%*
$D(Zn,H_2)$	700	343	345	375	8
	900	526	508	583	13
	1100	742	692	803	17
$D(Zn,He)$	700	289	266	372	28
	900	436	402	567	29
	1100	604	558	795	30
$D(Zn,N_2)$	700	-	91	81	-12
	900	-	138	127	-9
	1100	-	193	181	-7
$D(Zn,Ar)$	700	61	67	75	11
	900	107	105	118	11
	1100	166	151	169	11

C-E = Chapman-Enskog Theory

$$* = \frac{\text{theoretical (C-E) - experimental}}{\text{theoretical}} \times 100$$

Table 3.10 Diffusivities of Mercury in Inert Gases

$$\text{units} = \frac{D(\text{Hg,Carrier Gas}) \times 10^{-6}}{\text{m}^2\text{s}^{-1}}$$

	T/K	ref.28	expt.	C-E	%*
$D(\text{Hg},H_2)$	400	-	107	115	7
	500	-	150	172	13
	600	-	200	239	16
$D(\text{Hg,He})$	400	-	85	115	26
	500	-	121	168	27
	600	-	163	228	29
$D(\text{Hg},N_2)$	400	-	24	23	-4
	500	-	36	35	-3
	600	-	50	49	-2
$D(\text{Hg,Ar})$	400	23	20	20	0
	500	33	28	31	10
	600	44	38	44	14

C-E = Chapman-Enskog Theory

$$* = \frac{\text{theoretical (C-E) - experimental}}{\text{theoretical}} \times 100$$

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Chapter 4

Zinc Chloride

4.1 Introduction

There is a commerical interest in molten $ZnCl_2$ as a solvent and catalyst in the hydrocracking of coal slurries and heavy crude oil fractions[1]. Sulphur in the feedstock causes progressive poisoning of the melt by conversion to zinc sulphide. Several regeneration procedures have been employed including a fluidized-bed combustion[1] in which zinc chloride is distilled from relatively-involatile impurities. Although the vaporisation of zinc chloride has been extensively investigated[2-7] there remains an uncertainty of the published enthalpy and entropy changes for vaporisation. The most controversial aspect of these reports is the extent of polymerisation in the gas phase and the manner in which the extent varies with temperature. Neither vibrational spectra[8-10], both from matrix isolation studies and high temperature gas examination, nor mass spectrometry[3,7,11] provide unequivocal evidence for the presence of vapour dimers. Most thermodynamic results obtained from torsion effusion and transpiration, quasistatic vapour phase manometry are interpreted with the assumption that the vapour phase between 591 and 1200 K contains monomer and dimer only. Furthermore, two independent[3,5,6] careful manometric studies predict a quite different variation in dimer concentration with temperature in the vapour in equilibrium with the melt. The results of Keneshea and Cubicciotti[3] indicate the pressure fraction of dimer falls with increasing temperature whereas the most recent work of Polyachenok et al.[5,6] suggest the opposite.

The vaporisation has been re-examined in the temperature range 638 to 968 K by the modified entrainment method (MEM) in an attempt to resolve this uncertainty in the vaporisation thermodynamics and the variation of dimer concentration with temperature.

4.2 Structure of Zinc Chloride

Zinc Chloride, crystal

Until the mid-nineteen seventies it was widely accepted[12] that there were at least three distinct crystalline phases for zinc chloride, all stable (or metastable) at room temperature. Single crystal structures for three modifications (designated α, β and γ) have been reported by Brehler[13] in which the zinc is tetrahedrally co-ordinated by chlorine in each modification. Brehler refutes an earlier claim that the structure is one in which Zn is six-fold co-ordinated by Cl^-. In 1978, Brynestad and Yakel[14] prepared a scrupulously-anhydrous material which showed different X-ray reflexions from any of known patterns and further their phase pattern transforms to one or more of Brehler's phases if it is imperfectly protected from the atmosphere. The currently-accepted structure is orthorhombic, space group *Pna*2_1 ($Z = 4$), and consists of a hexagonal close packed lattice of Cl^- ions with the Zn^{2+} ions occupying one quarter of the available tetrahedral sites. Every Cl^- ion is common to two $ZnCl_4$ tetrahedron with bridging atoms in the vertices but with no shared faces or edges.

The long-standing uncertainty over the crystal structure is most likely due to the high affinity of $ZnCl_2$ for water and samples obtained from aqueous solution, even when carefully dehydrated, contain a small proportion of OH^- replacing Cl^- ions and this induces slip along the glide planes to generate structures based on cubic close packing. As much of the thermodynamic data for $ZnCl_2$ are pre-1970 it will be important to assess the significance of slight moisture contamination on such data. Further, new studies to determine (or redetermine) thermodynamic parameters must utilize anhydrous samples.

Molten and Glassy $ZnCl_2$

In recent years the chemistry and physics of molten and glassy $ZnCl_2$ have been widely studied[15,16,17] because of its unusual structural features and technological uses[1,12]. In the liquid phase near the melting point (T ≃ 591 K), $ZnCl_2$ shows a very high viscosity and a corresponding low electric conductivity. Furthermore it has been found that near the melting point its structure is similar to the glass phase[17].

The liquid phase structure has been investigated directly by neutron[15] and X-ray diffraction[18] and inferred from vibrational spectroscopic examination[19]. Addition of other chlorides e.g. $NiCl_2$, KCl to the system induce a marked decrease and increase in viscosity and conductivity respectively. These changes are interpreted in terms of extended network or lattice structures and may be represented as solid-like regions persisting into the liquid phase. As the temperature is increased these networks collapse producing smaller units e.g. $Zn_2Cl_6{}^{2-}$, $ZnCl_4{}^{2-}$, $ZnCl_3{}^{-}$, etc. and ultimately Zn^{2+} and Cl^-. Thus $ZnCl_2$ appears to melt over an extended range instead of displaying a sharp melting transition typical of a pure material. Moreover, in 1956, Craw and Rogers[20] noted published melting points varied between 239 and 365°C and reported the mp of their carefully-purified form as 318±2°C. Current editions of reputable textbooks and data compilations still report divergent results e.g. 275°C (Cotton and Wilkinson[21]), 283°C (CRC Handbook[22]). These variations may be explained by the presence of impurities in the $ZnCl_2$, particularly moisture, and the marked tendency for $ZnCl_2$ to supercool. An extended melting range is of course characteristic of a two component solid solution and the influence of OH^- incorporated within the lattice of the melting characteristics remains an open question.

The neutron diffraction study[15] performed at 600 K is less ambiguous. From integration of the appropriate radial distribution functions an average co-ordination of Zn^{2+} by Cl^- of 4.3±0.3 with an internuclear distance of 2.29±0.02 Å was found, a value very close to that found in the crystal. It was stressed that the mean 4-fold co-ordination of Zn^{2+} indicated by this study does not necessarily imply the existence of discrete covalent $ZnCl_4{}^{2-}$ ions, the four Cl^- represent a statistical time-average with rapid exchange with neighbouring ions. This study also eliminates $ZnCl^+$ and $ZnCl_3^-$ and the authors clearly state the most satisfactory model for liquid $ZnCl_2$ is in terms of Zn^{2+} and Cl^- only. They also examined samples that were deliberately contaminated with moisture (≃ 4% w/w) and found little change in the structure factors. The X-ray study[23] is supportive of the general conclusions outlined above from the neutron diffraction work.

The measurement of diffusion coefficients in strong aqueous solutions of $ZnCl_2$, corresponding to approximately $ZnCl_2 4H_2O$, are interpreted in terms of long-lived $ZnCl_4{}^{2-}$ ions[24]. Other physical properties of the melt are collected in Janz's "Molten Salt Handbook"[25] and recent studies by Angell et al.[26] and by Cacciola et al.[27].

4.3 Thermodynamic Properties of $ZnCl_2$ Condensed Phases

Table 4.1 shows the standard thermodynamic constants for $ZnCl_2$(c) taken from three critical compilations.

Table 4.1 Thermodynamic Properties of $ZnCl_2$(c) at 298.15 K

Year	ΔH_f^o kJ mol^{-1}	ΔG_f^o kJ mol^{-1}	S^o J K^{-1} mol^{-1}	C_p^o J K^{-1} mol^{-1}
1948[a]	-415.9	-369.4	108.4	75.6
1968[b]	-415.0	-369.4	111.5	71.3
1979[c]	-415.0	-369±12.6	111.5	67.4

[a] ref. 28, [b] ref. 29, [c] ref. 30.

Only C_p^o shows any significant variation (from 75.6 to 67.4 JK^{-1} mol^{-1}) and this most recent value derives from Cubicciotti and Eding[31] working in the range 300 to 1000 K. The fact that the remaining entries in the table show little change over a thirty year period does not necessarily mean they are well-established, only that they are based on early work.

Bates[32] measured the emf of the reversible cell at four temperatures in the range 25 to 40°C,

$$\text{Zn-Hg (2 phase amalgam)} \mid ZnCl_2(c) + \text{satd soln} \mid AgCl,Ag \qquad (4.3.1)$$

The cell reaction is

$$Zn(\text{amalgam}) + 2AgCl(c) = ZnCl_2(c) + 2Ag(c) \qquad (4.3.2)$$

and ΔG^o, ΔH^o and ΔS^o were extracted in the usual manner[32] from the cell emf. As most of the results in table 4.1 derive from this study it is worth noting

(i) hydrates of $ZnCl_2$ only precipitate below 28°C[12] so the 25°C measurement was on "metastable" $ZnCl_2(c)$; the continuity of the emf-temperature plot between 25 and 40°C indicates that the solid phase remained unhydrated down to 25°C.

(ii) independent work[33] had shown the cell emf for $Zn(c) \mid Zn^{2+}(aq) \mid Zn\text{-}Hg(5\%)$ was zero between 20 and 30°C and hence Zn(c) may replace Zn(amalgam) in the cell reaction above,

(iii) extraction of thermodynamic results for $ZnCl_2$

relies on corresponding results for AgCl; these are very well-established and

(iv) the enthalpy result comes from a first temperature derivative and is consequently much less precise than ΔG^{o}.

Wachter and Hildebrand[34] studied a similar cell with a molten electrolyte in the range 500 to 575°C. The fused electrolyte was carefully dried and handled. The cell reaction is of course the synthesis reaction from the elements and reduction of the results to 298 K using current C_{p}^{o} results[31] yield values which confirm Bates's earlier results.

The cell studied by Wachler and Hildebrand was again re-examined by Markov and Volkov[35] in 1963 and Robertson and Kucharski[36] in 1973 over a similar temperature range, 450 to 580°C and 450 to 600°C respectively. From the experimental section of both papers the cells were carefully prepared and the $ZnCl_2$ was kept anhydrous.

To conclude this section let us compare ΔG_{T}^{o} values for $Zn(l) + Cl_2(g) = ZnCl_2(l)$ from the four independent sources already mentioned (refs. 32, 34, 35, 36) in the temperature range 723 to 823 K (the mp of $ZnCl_2$ is 591±2 K, and for Zn is 693 K). Three of these four studies, all electrochemical, encompass this temperature range but Bates's work was at room temperature and the ancillary data taken from Barin and Knacke[37] are required to convert the results to the range of interest. Values of ΔG^o_T are collected in table 4.2.

Table 4.2 Free Energy of Formation of Zinc Chloride
$Zn(l) + Cl_2(g) = ZnCl_2(l)$ ΔG^o_T/kJ mol^{-1}

calculated from

$\Delta G^o_T = -370.39 + 85.77\times10^{-3}T$ Robertons[a] [723-873 K]

$\Delta G^o_T = -406.32 + 135.14\times10^{-3}T$ Markov[b] [723-853 K]

$\Delta G^o_T = -403.09 + 130.12\times10^{-3}T$ Bates[c] [room temp + ancillary data]

$\Delta G^o_T = -407.03 + 133.89\times10^{-3}T$ Hildebrand[d] [774-849 K]

T/K	Robertson[a]	Markov[b]	Bates[c]	Hildebrand[d]
723	-308	-309	-309	-310[e]
773	-304	-302	-303	-304
823	-300	-295	-296	-297

[a] ref. 36, [b] ref. 35, [c] ref. 32,
[d] ref. 34, [e] extrapolated

The agreement between Markov[35], Bates[32] and Hildebrand[34] is good, the maximum uncertainty being ≃

2 kJ mol^{-1} or 0.7%. However the most recent work by Robertson et al.[36], the free energy of formation differs significantly at high temperatures to ≃ 5 kJ mol^{-1} at 823 K. Hence their derived enthalpy and entropy results are not consistent with the three earlier studies, and must be regarded with caution.

The heat capacities of $ZnCl_2$(c and l) have been measured[31] in the range 298 to 750 K using a drop calorimeter. They report

$$C_p[ZnCl_2,c]/J\ K^{-1}mol^{-1} = 60.67 + 0.0230T\ [298<T/K<mp] \quad (4.3.3)$$

$$C_p[ZnCl_2,l]/J\ K^{-1}mol^{-1} = 100.8 \pm 10 \quad [mp<T/K<1000] \quad (4.3.4)$$

No temperature dependence was discerned for the liquid phase C_p result and this was probably due to the ready formation of a glass by $ZnCl_2$ on cooling below the mp (591 K). This glass formation[38] presents difficulties in the determination of the enthalpy of fusion, and experiments using an adiabatic calorimeter[31] gave 10.25 ± 0.21 kJ mol^{-1}, confirming a "lower limit" estimate from the drop calorimetry experiments. In an independent study[26] the enthalpy of fusion was determined to be 9.75 kJ mol^{-1}.

4.4 Vaporisation of Zinc Chloride

The total vapour pressures observed by Keneshea and Cubicciotti[3] for molten zinc chloride are in general agreement with those reported by other workers[2,6,39], but the conclusions about the molecular composition of the vapour are controversial. Vapour pressure measurements can be grouped as absolute which makes no assumptions as to the molecular weight of the vapour and non-absolute. For zinc chloride absolute measurements have been carried out by Keneshea and Cubicciotti (1964)[3] using a quasi-static method developed by Rodebush and Dixon[40]. They compared their absolute vapour pressure with the non-absolute values they obtained by transpiration measurements. The two methods will give the same results only if the vapour phase behaves as a perfect gas (a reasonable assumption at the temperature and pressures involved) and if the vapour species are known. They interpreted the differences between the two sets of measurements with the aid of their qualitative mass spectra analysis in terms of partial formation of dimeric species. From their results they concluded that the saturated vapour is principally monomeric but includes small amounts of dimeric molecules (Zn_2Cl_4) from 19% at 650 K to 4% at 850 K. Moss (1960)[41] combined his transpiration data with the boiling point data of Bloom et al.[42] and confirmed the presence of polymeric species in the vapour but concluded that the dimer species was the only significant polymer. Furthermore Topor and Moldovean (1972)[39] using similar quasistatic and transpiration techniques reproduced similar vapour composition results of Keneshea and Cubicciotti. This polymerisation was subsequently re-investigated by Polyachenok et al. (1976)[6] using a tensimetric method with a quartz membrane mill manometer. They concluded indirect contrast to the earlier workers, that the pressure fraction of the dimer species increased with increasing temperature, for example 1.2% at 650 K to 8.4% at 850 K.

Recently Skudlarski et al. (1987)[7] measured the mass spectrum and the vapour pressure over solid zinc chloride and compared their results (Knudsen-effusion + mass spectrometry) with the previous quasistatic and transpiration data. Extrapolating the vapour pressure of the dimer from Keneshea[3] and Topor[39] works to 570 K gives 4.4 x 10^{-3} mmHg and 5.3 x 10^{-3} mmHg respectively. This vapour pressure should readily be detectable by MS but surprisingly they failed to find the necessary ions characteristic of the dimer. This suggests that the enthalpy of vaporisation of the dimeric molecules is higher than that concluded by either Keneshea or Topor, but closer to Polyachenok results which indicates when extrapolated a relatively insignificant dimer pressure of 2.2 x 10^{-9} mmHg at

570 K.

Gregory and Rice (1968)[4] examined the zinc chloride vapour composition (temperature range 450-600 K) at a low electron ionizing potential (8 eV c.f. usual value 70 eV) on their mass spectrometer to decrease the chances of fragmentation of the dimer to the monomer. They also failed to observe a significant concentration of dimeric species. These workers conflict with the MS analyses by Kenshea (1964) [753 K][3] and Schäfer (1973) [555 K][11] who did detect the dimeric species. Furthermore Bloom et al. (1970)[12] based his transpiration vapour pressures and activities in molten zinc chloride mixtures on the analysis of the condensate of the vapour to be monomeric only. Further, the existence of higher mass zinc-chlorine species in the mass spectra may be explained in terms of ion-molecule reactions due to the vapour pressure of the source being too high for the spectrometer, for example, ions $ZnCl_2^+$, $ZnCl^+$ and Zn^+ may react with the monomeric species $ZnCl_2$ to produce the dimeric ions $Zn_2Cl_4^+$, $Zn_2Cl_3^+$ and $Zn_2Cl_2^+$ respectively. On closer inspection of Schäfer[11] and Rice[4] MS data gives the ionisation intensity ratio 100:13:7 and 100:11:6 respectively for $ZnCl_2^+$, $ZnCl^+$, Zn^+ and are remarkedly both consistent with each other. Schafer noted a further ion $Zn_2Cl_3^+$ which indicated a 1% dimer concentration at 555 K.

Electron diffraction data[43,44] in conjunction with the available spectroscopic evidence[45,46] reveals unambigously a linear configuration for zinc chloride monomer with the mean bond length (r_g):Zn-Cl, 2.05 ± 0.01 Å (ref. 43) and 2.072 ± 0.004 Å (ref. 44).

The infra-red absorption spectra of gaseous zinc chloride has been investigated by a low-temperature matrix isolation technique by Loewenschuss and co-workers (1968)[8]. The spectral analysis ranged from 800 to 35 cm^{-1} and four distinct regions were labelled a, b, c and d (see ref. 8, figure 1). Regions a (509-499 cm^{-1}) and d (101-76 cm^{-1}) were assigned to the monomeric species and b (293-255 cm^{-1} and 153-121 cm^{-1}) and c (101-76 cm^{-1}) to the dimeric species. They established from enriched zinc isotope experiments, the dimers had the correct intensity ratio and frequency for a four membered planar diamond shaped ring structure with two additional chlorine atoms located on the Zn-Zn axis. This structure (D_{2h}) had been directly observed and postulated earlier by McNamee[47], although several other infra-red active absorptions due to the dimer are predicted but none were observed. Further Loewenschuss et al.[8] showed qualitatively increasing the temperature of this effusion cell from 320 to 550°C decreases the concentration of the polymeric species in regions b and c. This supports the conclusion obtained from

Keneshea et al.'s[3,39,41] thermodynamic data. McNamee (1962)[47] studied the matrix isolation spectra of zinc chloride down to 250 cm^{-1} and observed similar absorption due to polymeric species. He concluded that dimers were present in the gas phase rather than artificially formed by thermal diffusion in the matrix. However in 1978, Givan and Loewenschuss[9] refuted this claim. Their infra-red spectra agree well with their earlier matrix-isolation results[8] except the bands previously assigned to aggregates could now be eliminated by lowering the deposition rate of the matrix.

Papathedorou (1979)[10] assigns the characteristic single strong polarised band from Raman gas-phase examination to be the symmetric vibration of the monomer at 702°C. This band has been observed in the infra-red by Givan and Loewenschuss[9]. Papathedorou speculates that his spectrum support a small deviation from linearity in the monomer (D_{∞} to C_{2V}). His results show a low signal-to-noise ratio which preclude any assignment of features due to polymeric species. Givan and Loewenschuss[9] have reported similar Raman spectra in other zinc halides which suggests that the zinc chloride dimer assignment is in the 200-170 cm^{-1} region.

Table 4.3 summaries the current argument for and against the existence of zinc chloride dimers in the gas phase. These have been classified into equilibrium (E) and non equilibrium (NE) methods. Notice that the existence of dimers is usually inferred from equilibrium measurement.

In summary there seems to be considerable evidence for the presence of dimers in the gas phase above liquid $ZnCl_2$, mostly by equilibrium methods. The heat of vaporisation of $ZnCl_2(l)$ and its ancillary thermodynamical data are discussed and compared with experimental MEM data in section 4.7 in an attempt to clarify the uncertainty in the vapour composition over $ZnCl_2(l)$.

4.5 Summary of Experimental Technique

The modified entrainment rig has been described in detail in chapter 2. Briefly, the sample (zinc chloride) is contained in a spherical quartz capsule approximately 1 cm in diameter suspended from one arm of a recording microbalance. The capsule orifice is in the form of a vertical capillary (ca. 20 mm long x 1 mm internal dia.); this acts as a diffusive resistance to the ingress of the downward flowing carrier gas (argon, 80 cm^3 (stp) min^{-1}) and the egress of the sample vapour. The experimental parameter is the rate of mass loss of the sample ($\mathring{\omega}$) at a preset temperature. Two separate capsules were used with capillary resistances $6.090 \times 10^4\ m^{-1}$ and $6.918 \times 10^4\ m^{-1}$, 192 experiment points in the temperature range

Table 4.3 Evidence For and Against the Existence of $Zn_2Cl_4(g)$

Technique		Supporting Dimer		Non-Suporting Dimer	
Mass Spectroscopy	(NE)	Keneshea	(1964) [753 K]^a	Rice	(1968) [450-600 K]^c
		Schafer	(1970) [555 K]^b	Skudlarski	(1987) [455-570 K]^d
IR and or Raman	(NE)	McNamee	(1962)^e	Loewenschuss	(1978) [455-570 K]^d
		Loewenschuss	(1968)^f	Papathedorou	(1979) ^{h} (E)
Transpiration and Absolute Measurements	(E)	Moss	(1960) [726-899 K]^i	Bloom**	(1970) [773-873 K]^k
		Keneshea	(1964) [684-869 K]^a		
		Rice*	(1968) [495-640 K]^c		
		Topor	(1972) [768-893 K]^j		
Tensimetric Study	(E)	Polyachenok	(1969) [773-1273 K]^l		
		Polyachenok	(1976) [775-1273 K]^m		
Modified Entrainment Method	(E)	Pang	(1988) [638-978 K]^n		

E = Equilibrium measurement NE = Non equilibrium measurement

^{a} ref. 3, ^{b} ref. 11, ^{c} ref. 4, ^{d} ref. 7, ^{e} ref.47, ^{f} ref. 8, ^{g} ref. 9,

^{h} ref. 10, ^{i} ref. 41, ^{j} ref. 39, ^{k} ref. 2, ^{l} ref. 5, ^{m} ref. 6 and n this work (see text)

* conclude dimer composition not more than 10%

** assume monomer vapour only in gas phase in molten chloride mixture.

638 ($\mathring{\omega} \approx 1.0 \times 10^{-12}$ kg s^{-1}) to 978 ($\mathring{\omega} \approx 8.7 \times 10^{-9}$ kg s^{-1}) K were recorded, 32 of these being with specially doped sample (see Appendix A4.3 for raw MEM data file).

4.6 Materials

Cyclic voltammetry was used to assay the purity of the zinc chloride melt. No significant peaks were observed due to electroactive impurities, but the small residual current was ascribed to water impurity and the amount estimated was about 0.002 mass per cent. For details of the bulk analysis see section 2.9. After loading the MEM rig with sample, the zinc chloride was further purified in-situ by vacuum drying whilst raising the temperature above its melting point for a period of more than 48 hours. Further purification was followed by passing dry hydrogen chloride over the melt for a least 18 hours followed by prolonged exposure to argon gas stream. As noted considerable care was invested in obtaining a high purity sample as one aspect of this study was to determine the effect of water contamination in the melt on the vaporisation thermodynamics.

4.7 Results and Discussion

The thermodynamics of the vaporisation of molten zinc chloride has been studied in the temperature range 638 to 978 K. The monomer and dimer equilibria were considered

$$ZnCl_2(l) = ZnCl_2(g) \quad [K_1],\ \Delta H_1^o,\ \Delta S_1^o \quad (4.7.1)$$

and

$$2ZnCl_2(g) = Zn_2Cl_4(g) \quad [K_2],\ \Delta G_2^o,\ \Delta S_2^o \quad (4.7.2)$$

and the rate of weight loss ($\mathring{\omega}$) assuming these are the only participating reactions is given by

$$\mathring{\omega} = \frac{D_1 A M_1 p^{\theta} K_1}{RT\ell}\left[1 + \frac{2D_2K_2K_1}{D_1}\right] \qquad (4.7.3)$$

where p^{θ} is the standard state pressure, M_1 is the molecular mass of the monomer and K_1 and K_2 are the respective equilibrium constants. Full derivation of the above equation is given in Appendix 2.2. The second term in parenthesis in the equation is the contribution made to the mass transport by the dimer. If the dimer concentration was considered negligible then the equation reduces to an evaporation of a single substance (zinc chloride monomer) in argon carrier gas, as shown in section 1.4. Also, as equation (4.7.3) describes the behaviour of a three component ($ZnCl_2$, Zn_2Cl_4, Ar) system the effects of multicomponent diffusion must be included. Consequently, D_i are the multicomponent diffusion coefficients of the ith component into the mixture; the estimation of D_i is described in section 3.4.

The results from this work were processed by two separate procedures; (i) in combination with other published work to establish the compatibility of literature thermodynamic results with this work and (ii) independently. By substitution of the equilibrium partial pressures of monomer (p_1^o) and dimer (p_2^o), the master equation (4.7.3) may be recast

$$\overset{\circ}{\omega} = \frac{AM_1}{RTl}\left\{D_1p_1^o + 2D_2p_2^o\right\} \qquad (4.7.4)$$

This equation may be solved simultaneously by substituting literature equations for total pressure ($P_T = p_1^o + p_2^o$) to give p_1^o and p_2^o separately over the common temperature range. Hence ΔH_1^o, ΔS_1^o, ΔH_2^o and ΔS_2^o are obtained by the appropriate regression.

Keneshea and Cubicciotti[3] quote

$$\log_{10}(P_T/\text{mm Hg}) = (9.550 \pm 0.085) - (6598 \pm 21)\text{K}/T \qquad [693\text{-}883\ \text{K}] \quad (4.7.5)$$

Polyachenok[5] et al. give

$$\log_{10}(P_T/\text{mm Hg}) = (8.866 \pm 0.012) - (6032 \pm 11)\text{K}/T \qquad [773\text{-}973\ \text{K}] \quad (4.7.6)$$

Topor[39] cites

$$\log_{10}(P_T/\text{mm Hg}) = (26.047\pm0.054) - (8122\pm46)\text{K}/T - 5.035\log_{10}T \quad [806\text{-}885\ \text{K}] \quad (4.7.7)$$

and Bloom[2] et al. give

$$\log_{10}(P_T/\text{mm Hg}) = 9.574 - (6639,8)\text{K}/T \quad [750\text{-}870\ \text{K}] \quad (4.7.8)$$

The total vapour pressure above molten zinc chloride using the above literature equations is compared in table 4.4. This table also includes expolorated data from Skudlarski et al.[7] and a derived set of data based on the MEM study (see later).

The vapour pressure in table 4.4 can be subdivided on closer inspection. At low temperature, the literature pressures are in general agreement to within acceptable experimental errors. However at higher temperatures, say 900 K, Polyachenok[5] and Topor[39] data are significantly lower than either Keneshea[3] or Bloom[2] data by more than 11 mmHg.

The MEM experimental thermodynamic constants for monomer vaporisation and dimerisation (equations (4.7.1) and (4.7.2)) were obtained by combining equation (4.7.4) with the literature vapour pressure data shown above which extracts the relevant monomer

Table 4.4 Vapour Pressure of Molten Zinc Chloride 650-1000 K

T/K	KC[a]	POLY[b]	TOPOR[c]	BLOOM[d]	SKUD[e]	MEM[f]
650	0.3	0.4	0.3	0.2	0.3	0.2
700	1.3	1.8	1.4	1.2	1.9	1.3
750	5.7	6.7	5.7	5.3	10.5	5.5
800	20.1	21.2	19.0	18.8	45.9	19.4
850	61.3	58.8	55.0	57.9	169.6	58.8
900	165.5	145.8	141.4	157.2	541.3	157.9
950	402.5	328.5	329.3	384.4	1529.3	382.2
1000	895.4	682.3	704.7	859.4	3894.3	846.8

Pressure units = mm Hg, Underlined figures = literature temperature range

[a] ref. 3, [b] ref. 5, [c] ref. 39, [d] ref. 2, [e] ref. 7 (455-570 K) Correlation not good with other workers [f] this work from Table 4.6 (part (al).

and dimer partial pressures and subsequent equilibrium constants (K_1 and K_2). Followed by a regression of $-RT\ln K_i$ vs. T, the gradient gives the (-) entropy value and intersection the enthalpy value of the equilibrium i considered (i = 1 or 2). These thermodynamic values are collected in table 4.5. The results for monomer vaporisation have been converted to a common temperature of 800 K using C_p for the liquid and gas quoted by Barin and Knacke[37] which were calculated to be

$$\Delta H_1^o(T_2)/\mathrm{J\ mol^{-1}}$$

$$= \Delta H_1^o(T_1) - 40.55\Delta T + 0.42\times10^{-3}(\Delta T)^2 \qquad (4.7.9)$$

$$\Delta S_1^o(T_2)/\mathrm{J\ mol^{-1}K^{-1}}$$

$$= \Delta S_1^o(T_1) - 40.55\ \ln\left[\frac{T_2}{T_1}\right] + 0.00084\Delta T \qquad (4.7.10)$$

where,

$$\Delta T = T_2 - T_1$$

Table 4.5 also includes the thermodynamic constants for equilibria K_1 and K_2 obtained independently by Keneshea[3], Polyachenok[6] and Topor[39].

It is clear from table 4.5 that the thermodynamic constants derived by combining the MEM data with the absolute vapour pressure measurements are dependent upon the chosen source of literature pressure equation used. Both Keneshea[3] and Polyachenok[6] thermodynamic

Table 4.5 Enthalpy and Entropy Changes* for Equilibria - Combined Sources

$ZnCl_2(l) = ZnCl_2(g)$, ΔH^o_1, ΔS^o_1 (all scaled to 800 K)

$2ZnCl_2(g) = Zn_2Cl_4(g)$, ΔH^o_1, ΔS^o_2

ΔH^o_1/kJ mol^{-1}	ΔS^o_1/J K^{-1} mol^{-1}	ΔH^o_2/kJ mol^{-1}	ΔS^o_2/J K^{-1} mol^{-1}	Range/K	Source This work - combined (MEM data) and ((Absolute Pressure)(Lit.))
128.8±1.5	130.2±1.9	-170±37	-207±47	693-883	(4.7.4) & ((4.7.5)(Keneshea))
99.6±12.	95.8±1.3	28±1.3	31±6	773-973	(4.7.4) & ((4.7.6)(Polyachanok))
177.5±2.8	114.9±3.2	-69±19	-72±22	806-885	(4.7.4) & ((4.7.7)(Topor))
133.0±2.1	134.4±2.6	-181±21	-214±26	750-870	(4.7.4) & ((4.7.8)(Bloom))
127.9±0.4	129.3	-168±17	-203±21	684-869	ref. 3 (Keneshea)
118.1±2.1	117.0±2.1	-84±3	-101±3	775-1273	ref. 6 (Polyachenok)
128.9±0.4	128.3±0.4	-149	-171	768-893	ref. 39 (Topor)

* the uncertainty intervals quoted are standard deviations from the linear regression of $\ln p_i$ vs. T^{-1}

results can be obtained. Not too surprisingly Topor's[39] vapour pressure equation coupled with the MEM data predicts Polyachenok thermodynamic constants since both absolute vapour pressure measurements (Polyachenok and Topor) are similar (see table 4.4), although Topor's own independent thermodynamic calculations clearly support Keneshea's work. Confusingly combining Polyachenok vapour pressure equation (4.7.6) with MEM data produces thermodynamic results which do not correlate well with their own or any of the published literature data. However the combined results obtained from either Keneshea or Bloom vapour pressure equations (4.7.5) and (4.7.8) with the MEM data agree well with Keneshea[3] and Moss[41] original investigation of zinc chloride.

It is readily shown that the temperature derivative of the dimer pressure fraction ($p_2^o/(p_1^o + p_2^o)$) is proportional to $(\Delta H_1^o + \Delta H_2^o)/T^2$ which is positive when substituting Polyachenok data[6] but negative using Keneshea et al.'s results[3]. This fact was utilized in the independent processing of the MEM study. The dimer pressure fraction at 900 K is ca. 2% from the results of Keneshea[3] and decreasing at higher temperatures. Hence it may be assumed that the dimer makes negligible contribution to the transport above 900 K and consequently the MEM results above this temperature (58 data points) were processed via the exact equation (1.5.1) assuming a two component ($ZnCl_2$ + Ar) system. This equation yields ΔH_1^o and ΔS_1^o only. These results when converted to the mid-point of the temperature range of the MEM data points below 900 K (102 points) were used with the master equation (4.7.3) to extract K_2 and hence ΔH_2^o and ΔS_2^o for a three component system (see table 4.6). Conversely Polyachenok's[6] data predicts the dimer fraction below 700 K to be less than ca. 2% and this procedure of first obtaining monomer thermodynamic data over a restricted temperature range to produce dimerisation results was again used (shown in table 4.6). This procedure is inconclusive, results close to those of Keneshea[3] and Polyachenok[6] can be obtained depending on the assumed temperature range selected for the negligible dimer fraction.

It is possible in principle to extract optimum values of ΔH_1^o, ΔH_2^o, ΔS_1^o and ΔS_2^o from the MEM results without making any assumptions about the extent of dimer contribution because there are 160 data points and 4 unknowns (ΔH_1^o, ΔH_2^o ...) several minimization routines from the National Algorithm Group[48] were explored but the results were unsatisfactory in that the convergence criteria were not met or absurd local minima were found. A simplex routine based on Nelder and Mead's algorithm[48] proved more satisfactory in minimizing the sum of the square of the differences of $\mathring{\omega}$ (experimental) and $\hat{\omega}$ (from equation (3)). Only points at temperatures below 856 K were used for which the transport function, ξ_i, is $\leqslant$ 0.1 and points were weighted as recommended by Kohman[49]. Some lack of robustness in the algorithm was apparent in that optimum values of ΔH_2^O and ΔS_2^O varied depending on the choice of the initial simplex but ΔH_1^O and ΔS_1^O were stable. No uncertainty intervals are obtained from simplex minimization routines as derivitization is not involved and the intervals quoted for the simplex results in table 4.6 reflects the range of minima located. It is clear that the MEM results derived by this simplex method are in satisfactory agreement with those of Keneshea[3], Topor[39] and Moss[41].

An independent check on ΔS_1^O can be obtained by combining McBride's[50] value of $S_{298}^O(ZnCl_2,c)$ with Cubicciotti and Eding's[31] $C_p(ZnCl_2,l)$, $C_p(ZnCl_2,c)$ and $\Delta S^O(ZnCl_2,c\rightarrow l)$ to give $S_{800}^O(ZnCl_2,l) = 208 \pm 2$ J K^{-1} mol^{-1}. Givan and Loewenschuss[9] derive statistical thermodynamic functions for $ZnCl_2(g)$ based on vibrational spectra of matrix isolated zinc chloride; $S_{800}^O(ZnCl_2\ g) = 335.9$ JK^{-1} mol^{-1}. Therefore ΔS_1^O (800) = 128 ± 2 J K^{-1} mol^{-1} in good agreement with the MEM results in table 4.6 and Keneshea et al[3].

Table 4.6 Enthalpy and Entropy Changes* for Equilibria - Independently

$ZnCl_2(l) = ZnCl_2(g)$, ΔH^o_1, ΔS^o_1 (all scaled to 800 K)

$2ZnCl_2(g) = Zn_2Cl_4(g)$, ΔH^o_2, ΔS^o_2

ΔH^o_1/kJ mol^{-1}	ΔS^o_1/J K^{-1} mol^{-1}	ΔH^o_2/kJ mol^{-1}	ΔS^o_2/J K^{-1} mol^{-1}	Range/K	Source
126.9±0.5	128.0±0.5	-162±8	-202±11	640-980	This Work[a](1)
120.±12.0	117.9±6.0	-96.6±4.8	-108.7±6.0	640-900	This Work[a](2)
128.5(±0.7)	130(±3)	-124(±23)	-220(±56)	640-890	This Work (Simplex)
(126.9)[b]	(128.0)[b]	-155±3	-180±4	640-890	This Work (doped sample)
127.9±0.4	129.3	-168±17	-203±21	684-869	ref. 3 (Keneshea)
118.1±21	117.0±21	-84±3	-101±3	775-1273	ref. 6 (Polyachenok)
132±0.3	132.9±1.0	-171.1±0.4	-195.8±0.4	726-899	ref. 41 (Moss)

* uncertainty interval (except for the Simplex results) are standard deviations of regression coefficients

[a] obtained by separating results into two temperatures which makes the assumption:

(1) dimer concentration negligible above 900 K, (2) dimer concentration negligiblebelow 700 K

[b] the results for the doped sample were all recorded below 900 K; consequently ΔH^o_1 and ΔS^o_1 were assumed for the pure sample in a(1)

Further it is obvious from the results collected in table 4.6 that the Russian values for ΔH^{o}_{2} and ΔS^{o}_{2} are almost exactly one half of the corresponding values of other workers. This does not appear to be a stoichiometry mistranscription as the Russian authors[6] comment explicitly on their low value of ΔS^{o}_{2} compared with Keneshea and Cubicciotti[3].

It is of some concern in the industrial exploitation of zinc chloride melts as hydrocracking solvents as to how a steady accumulation of water in the melt will affect the thermodynamic vaporisation constants. The water contamination can arise either from a damp feedstock or from the reduction of oxygen heteroatoms during cracking. For example, water has a marked effect[51] on the transport properties of melts and it has been established that the crystal structure[14] of zinc chloride at room temperature was doped in situ with water vapour to the extent of 0.3 mass per cent (2.3 per cent mole ratio). Increasing the temperature to just below the melting point resulted in the loss of about half of the added water. It is assumed that the residue remained in the melt. The fate of this water is uncertain. Zielke[1] reports that molten zinc chloride is resistant to hydrolysis, although recent investigations suggest otherwise (see section 2.9). Water is soluble in many melts[51] and, for example, water in 60:40 LiCl-KCl shows Henry's law behaviour up to 5 per cent mole ratio. Hydrolysis via $H_2O + Cl^- = OH^- + HCl$ and $H_2O + 2Cl^- = O^{2-} + 2HCl$ has been detected[52] in other halide melts. Thirty two data points were recorded for this artificially contaminated melt over the temperature range 640 to 864 K. Predictably, $\ln[\mathring{\omega}/\text{kg s}^{-1}]$ correlates well with T^{-1} ($r^2 = 0.998$) and the two linear regression lines, one obtained from the results of the pure sample and the other from the doped sample, were compared by analysis of covariance. This test showed there was no significant difference between the adjusted means or the regression coefficients and consequently it is highly probable that the results derive from the same population. Hence water doping of $ZnCl_2$ at the one per cent molar ratio level has no effect on the thermodynamics of vaporisation. Table 4.6 shows the thermodynamic constants ΔH_2^o and ΔS_2^o using the monomer constants of zinc chloride already calculated in the same table.

4.8 Conclusion

From both simplex routine and by using independent ancillary thermodynamical data, the enthalpy and entropy values of equilibria (equation (4.7.1) and 4.7.2)) shows the proportion of dimer in the equilibrium vapour above molten zinc chloride to decrease with increasing temperature. This is at variance with the most recent examination[5,6] of this system but supports earlier studies[3,39,41]. Subsequently the vapour pressure equations for monomer and dimer over molten $ZnCl_2$ are based on this criterion

$$ZnCl_2(l) = ZnCl_2(g) \qquad (4.8.1)$$

$$2ZnCl_2(l) = Zn_2Cl_4(g) \qquad (4.8.2)$$

and may be derived from the results in table 4.6(al) and are

$$\ln[p_1/P^\theta] = -(15300 \pm 60)K/T + (15.39 \pm 0.06) \quad [640-980\ K] \qquad (4.8.3)$$

$$\ln[p_2/P^\theta] = -(11000 \pm 970)K/T + (6.5 \pm 1.3) \quad [640-980\ K] \qquad (4.8.4)$$

$$[P^\theta = 101325\ N\ m^{-2}]$$

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Chapter 5

Thermodynamics of (i) the Dissociative Sublimation of Zinc Sulphide and (ii) Zinc Sulphide Transport in Hydrogen Chloride by Modified Entrainment.

Notation for Chemical Equilibria Used Throughout Chapter 5

Reductive Sublimation of Zinc Sulphide in Hydrogen

$ZnS(c,\beta) + H_2(g) = Zn(g) + H_2S(g)$ K_1 [5.1]

$ZnS(c,\alpha) + H_2(g) = Zn(g) + H_2S(g)$ K_2 [5.2]

Dissociative Sublimation of Zinc Sulphide

$ZnS(c,\beta) = Zn(g) + \frac{1}{2}S_2(g)$ K_3 [5.3]

$ZnS(c,\alpha) = Zn(g) + \frac{1}{2}S_2(g)$ K_4 [5.4]

Formation of Hydrogen Sulphide

$H_2(g) + \frac{1}{2}S_2(g) = H_2S(g)$ K_5 [5.5]

Zinc Sulphide transported in Hydrogen Chloride

$ZnS(c,\beta) + HCl(g) = ZnCl_2(l) + H_2S(g)$ K_6 [5.6]

$ZnS(c,\beta) + HCl(g) = ZnCl_2(g) + H_2S(g)$ K_7 [5.7]

Dimerisation of Zinc Chloride

$2ZnCl_2(g) = Zn_2Cl_4(g)$ K_8 [5.8]

5.1 Introduction

Zinc sulphide exists in two principal forms, Sphalerite (β, cubic or 3C) and Wurtzite (α, hexagonal or 2H). The low temperature form is β-, the transition temperature[1] is 1293±10 K, giving the α-form which is metastable at room temperature.

The crystal structure of ZnS(β) is best considered as a cubic close-packed array of sulphide ions, with Zn^{2+} occupying one half of the tetrahedral holes. ZnS(α) has the same structure except that the sulphide ions are now in hexagonal close-packed array. Both zinc and sulphur are "four co-ordinated" in both structures and the Zn-S distance is 2.35Å in ZnS(β) and 2.36Å in ZnS(α). Cubic close packed structures containing the repeating sequence of layers ---ABCABCABC---, whereas hexagonal close packing involves the sequence, ---ABABABAB---, both arrangements being equally economical in terms of space filling[2]. From this description it is clear that a local transformation from ccp to hcp requires translation via a glide plane with a modest activation energy. Since 1950, polytypism[3] has been recognised in ZnS, the polytypes possessing crystallographically structures containing regular sequences of mixed cubic and hexagonal close packing. These polytypes should not be conceived as the α or β polymorphs containing random glide dislocations but unique structures with long range order, the repeating unit often exceeding several tens of layers.

Interconversion of sphalerite into various polytypes and wurtzite, may be induced by mechanical effects[4] (e.g. vitromilling), temperature change[5] and the presence of impurities[3]. The ease of transformation is probably strongly influenced by surface effects[6], the appearance of metastable phases increasing as the particle size becomes smaller.

The formation of polytypes must be suspected whenever ZnS is formed under conditions of mechanical stress, in the presence of impurities or at high temperatures where local temperature fluctuations induce dissociative sublimation and recondensation cycles involving small crystallites. With the exception of mechanical stress, these are all conditions likely to be encountered during the formation of ZnS in this work. Hence care was taken to determine the composition of the higher temperature phases used in this work by X-ray diffraction.

The modified entrainment method has been used to study two principal systems

i) the dissociative sublimation of both α- and β-zinc sulphide, $ZnS(c) = Zn(g) + \frac{1}{2}S_2(g)$ [5.3] and [5.4], in the temperature range β- (1012 to 1271 K) and α- (1300 to 1443 K), and the appropriate free energy equations derived.

ii) equilibrium [5.7], the transport of $ZnS(\beta)$ in HCl, has also been examined between 1023 and 1263 K to yield thermodynamic data. These results when combined with free energy data for the vaporisation of zinc chloride (see chapter 4) yield a definitive free energy equation for [5.6] within the liquid range of zinc chloride, 591 to 1005 K.

5.2 Experimental

Zinc Sulphide

The modified entrainment method has been described in detail in chapters 1 and 2. Three different capsules were used with capillary resistances from 1.912×10^4 to 2.132×10^4 m^{-1}. For $ZnS(\beta)$, 92 data points were recorded with $\mathring{\omega}$ ranging between 7.4×10^{-12} kg s^{-1} (at 1012 K) to 2.8×10^{-10} kg s^{-1} (at 1271 K). For $ZnS(\alpha)$, 199 data points were noted from 1300 K ($\mathring{\omega} \simeq 3.6 \times 10^{-10}$ kg s^{-1}) to 1433 K ($\mathring{\omega} \simeq 1.6 \times 10^{-9}$ kg s^{-1}).

Zinc Sulphide in Hydrogen Chloride

Two separate capsules were used with diffusive resistances of 6.699×10^4 and 6.006×10^4 m^{-1}. The experimentally-determined quantity is the rate of mass loss of ZnS from the capsule at a known temperature, $\mathring{\omega}(T)$. Four doping ratios of hydrogen chloride in argon (between 0.0602 and 0.0968) were used and are quoted as pressure fractions $(p_{HCl}/(p_{Ar} + p_{HCl}))$ determined from a ratio of flow rates of Ar and HCl from calibrated mass flow controllers reading in cm^3(stp) min^{-1}. The total flow rate (Ar + HCl) was ca. 100 cm^3 (stp) min^{-1} and 145 data points were recorded from 1023 K ($\omega \simeq 1.2$ x 10^{-10} kg s^{-1}).

5.3 Materials (see table 2.2 manufacturer's specifications)

Zinc sulphide was used without further purification (Aldrich Gold Label, 99.99%). Surprisingly, it was common to lose several mass per cent of volatile material during initial heating. The sample was characterized by emission spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis (TGA), mass spectrometry (MS) and elemental analysis. Trace metallic impurities were determined by emission spectroscopy and were present at the following concentrations: Cd, 10 ppm; Na, 10 ppm; Pt, 2 ppm; Mo, 1 ppm; Ca, < 1 ppm; Mg < 1 ppm. XRD showed the sample to be 95+% sphalerite. It has been reported[7] that ZnS is slowly oxidised to $ZnSO_4$ in moist air and that the freshly precipitated material adsorbs water which gives a continous dehydration loss on drying. Sulphate was shown to be absent from both the stock material and heated samples. TGA (Perkin Elmer TGS-2) in flowing nitrogen from 300 to 973 K at 20 K min^{-1} showed a near-linear mass loss of 2.95 mass % terminating between 920 and 970 K. The dissociation pressure above ZnS at 1000 K is ca. 5 x 10^{-5} mmHg so no significant contribution was expected from dissociative sublimation. MS(AEl MS 30) with a solid injection probe was used to identify the volatile species. The sample was heated from ca. 350 to 623 K while continously monitoring the mass spectrum in the m/e range 14 to 220. Water was noted at all temperatures, the maximum evolution being at ca. 450 K and decreasing thereafter. H_2S was observed from 480 K rising to a maximum at 540 K and decreasing thereafter. SO_2, in smaller quantities, was also observed at temperatures in excess of 480 K. No other volatile material that originated from the sample was detected. The H_2S probably arises from the reaction $3S + 2H_2O = 2H_2S + SO_2$ which is known to proceed slowly on boiling S in H_2O (the sample was slightly sulphur-rich, see below). Elemental analysis showed the stock material to have a Zn:S ratio of 0.993 ± 0.002. It has been suggested[8] that the stability of sphalerite depends on it being slightly S-rich but the non-stoichiometry range is small, 0.998 ± 0.001. In summary, the stock material was contaminated with both moisture and sulphur and has a composition $ZnS_{1.007 \pm 0.002}$ 0.168 H_2O). These impurities have negligible influence on the MEM results as the minimum temperature for the MEM study was 1010 K by which temperature the impurities were lost by volatilization. This was confirmed by

Table 5.1 The XRD and Analytical Analysis on Heated Samples of ZnS(β) at 700 to 1230°C to Simulate MEM Conditions

Stock Sample at °C	Sphalerite (β)	Wurtzite (α)	Zn:S ratio
Ambient	dominant	<5%	0.993±0.002
700^a	dominant	<5%	0.998±0.002
800^a	dominant	<5%	-
900^a	dominant	≃5%	0.999±0.002
900^b	dominant	5-10%	-
1100^c	minor	dominant	0.999±0.002
1130^d	trace	dominant	-
1230^e	trace	dominant	-

a, for 24 h in H_2, b, for 32 days in Ar followed by 10 min H_2 (hydrogen cannot be used for long periods at high temperatures because of transport by reductive sublimation), c, for 14 days in Ar, d, heated to 1130°C and cooled to 900°C (10 K min^{-1}/N_2) and e, heated to 1230°C 20 K min^{-1}/N_2

5.4 Results and Discussion

Sublimation of Zinc Sulphide at 1000-1400 K

An attempt was made to measure the enthalpy of transition directly using differential scanning calorimetry (DSC, Standard Redcroft Model 1500). The results were ambiguous; there was a slow endotherm with an onset of 1173 K which merged into a more rapid exotherm which was completed at 1333 K (see figure 5.1). It is not possible to deconvolute the two features and only speculation may be offered as to the structural changes that are responsible for these features. These results suggest that the data points from modified entrainmnent above 1173 K with the β-phase should be treated with caution. An X-ray diffraction study of the $\beta \rightarrow \alpha$ phase transition has been reported by Baars and Brandt[5] who steadily heated a "weakly disordered cubic" phase from 293 K while monitoring the diffraction pattern. At about 1173 K, the residual disorder decreases until 1273 K it had been eliminated. Above 1273 K there was a rapid, quantitative conversion to the hexagonal phase, with complete conversion at 1400 K. The implication of this study on our reported enthalpy and entropy of transition is considered overleaf in the Modified Entrainment section.

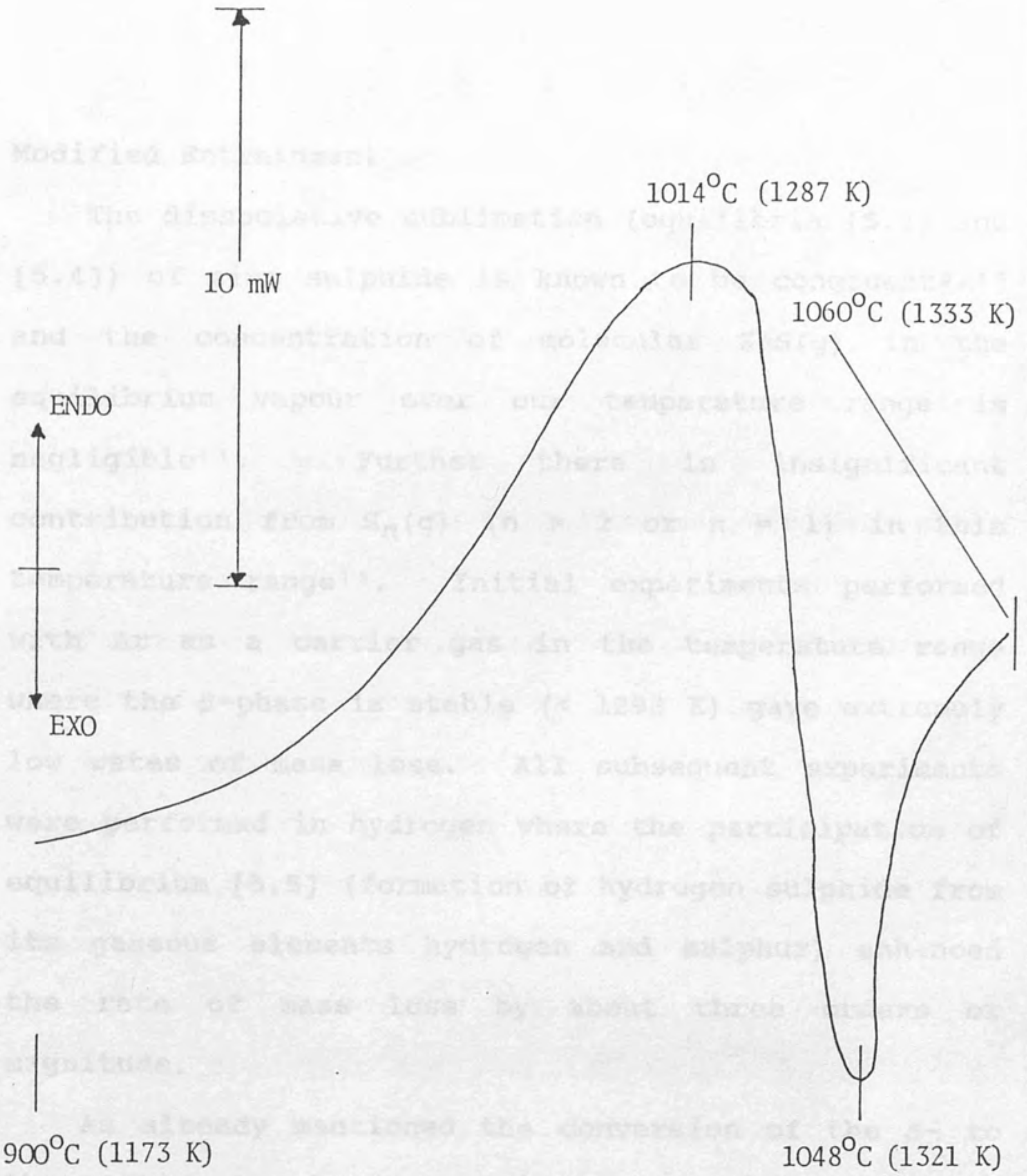

Figure 5.1 A DSC Trace for ZnS from 900 to 1100°C

Scan speed = 5 K min^{-1}
Atmosphere = flowing nitrogen, 50 cm^3 min^{-1}
Baseline drift = 5 mW over 200°C

Modified Entrainment

The dissociative sublimation (equilibria [5.3] and [5.4]) of zinc sulphide is known to be congruent[9,10] and the concentration of molecular ZnS(g) in the equilibrium vapour over our temperature range is negligible[11]. Further there is insignificant contribution from $S_n(g)$ ($n > 2$ or $n = 1$) in this temperature range[12]. Initial experiments performed with Ar as a carrier gas in the temperature range where the β-phase is stable (< 1293 K) gave extremely low rates of mass loss. All subsequent experiments were performed in hydrogen where the participation of equilibrium [5.5] (formation of hydrogen sulphide from its gaseous elements hydrogen and sulphur) enhanced the rate of mass loss by about three orders of magnitude.

As already mentioned the conversion of the β- to the α-phase has been extensively investigated and the effects of impurity levels[3,13], particle size[6], mechanical stress [4], etc., on both the rate and temperature of conversion is well-documented. The conversion is facile and it was clearly necessary to establish the identity of the material used in modified entrainment, especially in the region ca. 100 K below the transition temperature, where a slow conversion to the α-phase could invalidate the experiments.

Accordingly batches of stock ZnS were heated in flowing H_2, N_2 or Ar for at least 24 hours, to simulate their behaviour in the modified entrainment rig, quenched rapidly and examined by X-ray diffraction (XRD). Sample sizes and irradiation times were such that the level of discrimination between the phases was about 5%. Table 5.1 summarises the sample treatment.

Further, two separate modified entrainment experiments on the β-phase were completed with different initial samples and different temperature sequences; in one set the temperature was increased steadily from 1120 K to within 50 K of the transition temperature and decreased to 950 K, recording 55 data points ($\omega(T)$) at regular intervals. For the second set, the temperature was decreased from 1150 to 910 K, then increased to 1250 K, noting 37 values of $\omega(T)$. An analysis of covariance on the regression lines (ΔG^{O}_{3}/J mol^{-1} vs. T/K) showed no significant difference. For experiments with the α-phase, zinc sulphide was maintained at 1440 K in H_2 for at least two hours to ensure complete conversion.

Only two of the equilibrium constants K_1, K_3 and/or K_5 are independent and it is convenient to write the flux equations in terms of K_3 and K_5. Hence knowing the hydrogen sulphide equilibrium constant K_5 (obtained from standard tables), K_3 (the sublimation of zinc sulphide) may be obtained from

$$K_3 = \left[\frac{\varpi R T \ell}{M_{ZnS} A}\right] / (D_{Zn} D_{H_2S} K_5 \ p^{\theta} P) \qquad (5.4.1)$$

In this equation, ϖ is the rate of mass loss of ZnS, ℓ/A is the length over the cross-sectional area (the diffusive resistance) of the capillary, M_{ZnS} is the molecular mass of ZnS, D_i are the quaternary diffusion coefficients, K_i are equilibrium constants, p^{θ} is the standard state pressure (101325 N m^{-2}) and P is the working pressure in the MEM rig (usually atmospheric + 2.3 mmHg). The equilibrium constants and numerical notation is shown at the beginning of the chapter and is used throughout. The diffusion coefficients (D_i) include a power law dependence on temperature and are formulated in terms of the corresponding binary diffusion coefficients ($\mathcal{D}_{ij}$) into the majority component (H_2) and a multicomponent diffusion correction term (γ_i). The derivation of equation (5.4.1) and the form of γ_i are outlined in the Appendix A2.3 and in section 3.4.

Use of equation (5.4.1) implies a knowledge of K_5 (formation of gaseous hydrogen sulphide) and its temperature dependence. The thermodynamic parameters for the components in K_5 are well established[12] and values of free energy equation ΔG_5° were calculated at

100 K intervals from 900 to 1500 K using equation (5.4.2)

$$\Delta G^{o}_{5} = \Delta H^{o}_{298} - T\Delta(\mathrm{fef}) \qquad (5.4.2)$$

$$\text{where fef} = -\,(G^{o}_{T} - H^{o}_{298})/T \qquad (5.4.3)$$

calculated JANAF[12] data form ΔH^{o}_{298} and $\Delta(\mathrm{fef})$. Regression of these results with T yielded

$$\Delta G^{o}_{5}/\mathrm{J\ mol^{-1}} = (-90333\pm110) + (49.3\pm0.1)T \quad [900\text{-}1500\ \mathrm{K}] \qquad (5.4.4)$$

The uncertainty intervals are standard deviations of the regression coefficients. A recommended expression[14] for this equilibrium [5.5] over a much wider temperature range (298 to 1750 K) agrees with (5.4.4) to within 0.2% at 900 K and to within 3.3% at 1440 K, the upper temperature limit in this work.

The results from two independent MEM experimental data with ZnS(β) using capsules with different channel dimensions were pooled, the sublimation of zinc sulphide equilibrium constant K_3 extracted from equation (5.4.1), and ΔG^{o}_{3} regressed with T to yield an equation in the form of (5.4.4). A statistical routine was used which identified outliers (data pairs for which the standardized residual > |2|), which were then rejected, the rejection sequence terminating when $r^2 = 0.998$ ($n = 76$). The initial r^2 was 0.995 for all data points ($n = 92$), where r = correlation coefficient.

$$\Delta G^{\circ}_{3}(\beta)/\mathrm{J\ mol^{-1}} = (374200 \pm 1200) - (190.4 \pm 1.1)T \qquad [1012\text{-}1271\ \mathrm{K}] \quad (5.4.5)$$

A similar procedure was adopted for the experiments with the α-phase when the results from three separate experiments with the same capsule were pooled ($n = 199$, $r^2 = 0.997$), the final regression equation being based on $n = 191$.

$$\Delta G^{\circ}_{4}(\alpha)/\mathrm{J\ mol^{-1}} = (376700 \pm 900) - (191.9 \pm 0.6)T \qquad [1300\text{-}1440\ \mathrm{K}] \quad (5.4.6)$$

In both cases the rejected data points were randomly distributed throughout the temperature range; the uncertainty intervals in equations (5.4.5) and (5.4.6) are standard deviations of the regression coefficients (see table 5.2). Assuming that these equations may be extrapolated to the transition temperature (1293 K) which is equivalent to the approximation,

$$\Delta C_p^{\beta}(1010\text{-}1293\ \mathrm{K}) = \Delta C_p^{\alpha}(1293\text{-}1440\ \mathrm{K})$$

the transition of $(\beta \rightarrow \alpha)$ give rise to the experimentally determined thermodynamical data of enthalpy and entropy

$$\left.\begin{aligned} \Delta H^{o}\ (\beta \rightarrow \alpha)1293 &= -2.5 \pm 1.5\ \mathrm{kJ\ mol^{-1}} \\ \Delta S^{o}(\beta \rightarrow \alpha)1293 &= -1.5 \pm 1.3\ \mathrm{J\ K^{-1}\ mol^{-1}} \end{aligned}\right\} \quad (5.4.7)$$

The heat capacities for $ZnS(\alpha)$ and $ZnS(\beta)$ at both high[16] and low[15] temperatures have been reported by the Bureau of Mines (USA) group. The high temperature work revealed no enthalpy of transition and the results in combination suggest an athermal transformation

$$\left.\begin{aligned} \Delta(H^{o}_{1300}-H^{o}_{298})(\beta \rightarrow \alpha) &\simeq 0\ \mathrm{kJ\ mol^{-1}} \\ \Delta S^{o}(\beta \rightarrow \alpha)1300 &\simeq 0.4\ \mathrm{JK^{-1}\ mol^{-1}} \end{aligned}\right\} \quad (5.4.8)$$

Hence the results from this work are in satisfactory agreement with the Bureau of Mines (BM) study.

A recent careful examination[17] of a high temperature solid electrolyte cell yielded Gibbs free energies for the reversible cell reaction,

$$ZnS(\beta) + 3Cu_2O(c) = ZnO(c) + 6Cu(c) + SO_2(g) \quad (5.4.9)$$

Table 5.2 Results of Linear Regression on Five Different Data Sets, Separately and in Combination; $\Delta G^{o} = A - BT = \Delta H^{o} - T\Delta S^{o}$

$ZnS(c,\beta,\alpha) = Zn(g) + \frac{1}{2}S^{2}(g)$ K_3 and K_4

Data Set Code	n	n*	ZnS phase	A+ J mol⁻¹	B+ J mol⁻¹ K⁻¹	Range/K
C	55	43	β	374215±1457	190.6±1.2	
E	37	33	β	373883±1765	190.2±1.5	
D	90	90	α	377917±1383	192.7±1.0	
F	62	62	α	378113±1127	192.6±0.8	
G	47	39	α	375024±1377	190.9±1.0	
C+E		76	β	374174±1148	190.4±1.1	[1010-1270]
D+F+G		191	α	376746±874	191.9±0.6	[1300-1440]

\+ the uncertainty intervals in A and B are one standard deviation

n-n* number of rejected data pairs

* the standardised residual is the residual of the i_{th} observation over its standard deviation

which in combination with ancillary thermodynamic data gave a similar zinc sulphide sublimation free energy equation

$$\Delta G^{\circ}_{3}(\beta)/\mathrm{J\ mol^{-1}} = 387000-199T \quad [1180-1210\ \mathrm{K}] \qquad (5.4.10)$$

Over the common temperature range the experimental MEM results (5.4.5) for $\Delta G^{\circ}_{3}(\beta)$ are about 2% low compared with those from the literature equation (5.4.10) but the constants are quite different suggesting internal compensation. A comparison of ΔG°_{3} and ΔG°_{4} from several sources is given in table 5.3.

The constants A and B in the free energy equations (5.4.5) and (5.4.6) of the dissociative sublimationn of zinc sulphide correspond to the enthalpy and entropy changes respectively at the mid-points of the experimental temperature ranges. The experimental results may be re-converted to apply to the standard formation reaction (5.4.11) at 298 K,

$$\mathrm{Zn(c) + S(rhomb) = ZnS}(\alpha,\beta) \qquad (5.4.11)$$

using supplementary thermodynamic data for zinc[20], sulphur[12] and zinc sulphide[16]. These second-law conversions yield heats of formation of

$$\Delta H^{\circ}_{f}[\mathrm{ZnS},\beta]298 = -190.2\pm4.6\ \mathrm{kJ\ mol^{-1}} \qquad (5.4.12)$$

Table 5.3 A comparison of literature data for the Equilibrium

$$ZnS(\alpha,\beta) = Zn(g) + \tfrac{1}{2}S_2(g),\ \Delta G^{o}_{3/4}/J\ mol^{-1} = A - BT$$

Phase	Range/K	A	B	Source
β	1180-1210	387000	199	ref. 17 (Schaefer)
β	1180-1210	391200	201	ref. 18 (Richards)
β	< 1293	374300	193	ref. 19 (Rosenqvist)
β	1010-1270	374200	190	this work
α	1323-1473	360900	183	ref. 19 (Rosenqvist)
α	1300-1440	376700	192	this work

$$\Delta H_f^O[ZnS,\alpha]298 = -196\pm4.0 \text{ kJ mol}^{-1} \qquad (5.4.13)$$

Where the uncertainty intervals are ±2 (standard deviation) the usual practice for ΔH_f^O (see table 5.4).

The MEM results were also processed by the third-law method. Here, the complete data set of $\mathring{\omega}(T)$ is used (92 points for the β-phase and 199 points for α-), each data pair yielding a value for K_3 or K_4 from equations [5.3] and [5.4] respectively. Equation (5.4.14) is then used to derive a set of values for ΔH^O_{298}

$$\Delta H_n^O(\alpha,\beta,298) = T\Delta[-(G_T^O-H_{298}^O)/T] - RT\ln K_n \qquad (5.4.14)$$

where n = 3 or 4.

Gibbs free energy functions for ZnS were calculated from the heat capacities and derived functions reported Zn(g) were taken from Hultgren[20] and for S_2(g) from the JANAF compilation[12]. Finally, combining with $\Delta H_f^O[S_2,g] = 128\pm0.29^{12}$ kJ mol^{-1} and $\Delta H_f^O[Zn,g] = 137.74\pm0.42^{20}$ kJ mol^{-1}, standard enthalpies of formation corresponding to equation (5.4.11) are derived (see table 5.5). These are then compared with the second law values in table 5.6.

Notwithstanding the identification of our low temperature phase as 95+% β by XRD (see table 5.1), Samelson and Brophy[13] maintain that chemically-pure ZnS(β) always contains stacking faults, mostly arising from twinning. Aminoff and Broomé[21] have shown that α-ZnS exists in the vicinity of the interfacial planes of cubic twin. The experiments of Baars and Brandt[9] referred to earlier in the discussion of our DSC results suggest that the concentration of the α-phase in a weakly disordered cubic phase could be ca. 20%. The DSC results (see figure 5.1) show a feature that occurs in the same temperature interval (900-1020°C) that Baars and Brandt[5] note annealing of the residual disorder in this weakly disordered cubic phase. Together, this evidence may suggest our transition data could refer to the process $(0.8\beta + 0.2\alpha)\rightarrow\alpha$ rather than $\beta\rightarrow\alpha$ however unlikely. This introduces an additional uncertainty into the transition data and all results specific to the β-phase. The error limits quoted reflect this additional uncertainty.

Table 5.4 Zinc Sulphide Second Law Treatment

$$\begin{tikzcd}
ZnS(\beta) \arrow[r, "\Delta H_T^o"] & Zn(g) & + & \tfrac{1}{2}S_2(g) & <1141\ K> \\
& Zn(g)(1180K) \arrow[u, "e"] & & & \\
& Zn(l)(1180K) \arrow[u, "d"] & & \tfrac{1}{2}S_2(g)(298\ K) \arrow[uu, "h"] & \\
& Zn(l)(693K) \arrow[u, "c"] & & & \\
& Zn(c)(693K) \arrow[u, "b"] & & & \\
ZnS(\beta) \arrow[uuuuu, "i"] \arrow[r, "\Delta H_f^o"] & Zn(c) \arrow[u, "a"] & + & S(rhombic) \arrow[uuu, "f"] & <298\ K>
\end{tikzcd}$$

Completing the thermodynamic cycle, the standard formation of Zinc Sulphide ΔH_f^o (298) is obtained.

$$\begin{aligned} \Delta H_f^o\ / &= i + \Delta H_T^o - (a+b+c+d+e+f+h) \\ &= (43.5\pm0.2) + (374.2\pm2.2) - (227.4\pm0.8) \\ &= 190.2\pm2.3 \end{aligned}$$

for a→e see Hultgren ref. 20, ΔH_T^o experimental

f→h JANAF ref. 12 result eqn. (5.4.5)

i Pankratz ref. 16

Table 5.5 Zinc Sulphide Third Law Treatment

$$\begin{tikzcd}
ZnS(c,\beta,\alpha) \arrow[r, "\Delta H_S^o"] \arrow[dr, "\Delta H_f^o"'] & Zn(g) & + & \tfrac{1}{2}S_2(g) & <298\ K> \\
& Zn(c) \arrow[u, "a"'] & + & S(rhombic) \arrow[u, "b"'] & <298\ K>
\end{tikzcd}$$

Dissociative Sublimation of zinc sulphide at 298 K

$\Delta H_S^o(298)/kJ\ mol^{-1} = \Delta G_T^o + T\Delta(fef)$

The heat of formation of zinc sulphide may now be derived

$\Delta H_f^o(298)/kJ\ mol^{-1} = \Delta H_S^o(298) - (a+b)$

for " $\beta = 395.99 - 201.99 = 194.0 \pm 0.7$

" $\alpha = 398.29 - 201.99 = 196.5 \pm 0.5$

where

ΔG_T^o obtained from MEM experimental raw data of eqn. (5.4.5)

$\Delta(fef) = (fef)_{Zn(g)} + \tfrac{1}{2}(fef)_{S_2(g)} - (fef)_{ZnS(c)}$

from ref. 12, 20 and 15, and 16.

The free energy functions (fef) derived are

$\Delta(fef)_\beta/kJ\ mol^{-1} = 915.84 - 34.652 \times 10^{-3}T$

[1000-1300 K]

and

$\Delta(fef)_\alpha/kJ\ mol^{-1} = 912.99 - 32.384 \times 10^{-3}T$

[1200-1500 K]

Table 5.6 Comparison of Second Law and Third Law Enthalpies of Formation of Zinc Sulphide at 298 K

$Zn(c) + S(rhomb) = ZnS(\alpha,\beta)$

	2nd Law	3rd Law
$ZnS(\beta)$/kJ mol^{-1}	-190.2 ± 4.6	$-194.0\pm0.7^*$
$ZnS(\alpha)$/kJ mol^{-1}	-196.4 ± 4.0	$-196.3\pm0.5^*$
$\Delta H_f^o(\beta\to\alpha)$/kJ mol^{-1}	-6.3 ± 6.1	-2.3 ± 0.9

* the uncertainty intervals quoted for the 3rd Law results are ±2 (standard deviations of mean.

5.5 Results and Discussion

Zinc Sulphide Transport in Hydrogen Chloride

The H_2S produced in reaction [5.7] is significantly dissociated (K_5(1200 K) ≃ 500) in the experimental temperature range (1023-1263 K). The H_2 being produced from the dissociation participates in reductive sublimation of ZnS. Further, $ZnCl_2$ undergoes slight dimerization below 1200 K as shown in the previous chapter. The equations [5.3], [5.5], [5.7] and [5.8] were considered as the only participating equilibria during entrainment. Notice that the reductive sublimation of zinc sulphide with hydrogen [5.1] referred to the above arises from the combination of zinc sulphide sublimation [5.3] and hydrogen sulphide reaction [5.5], consequently it is not included explicitly.

The central assumption of the modified entrainment method (MEM) is that the diffusive resistance offered by the capillary above the sample is sufficiently high so that the equilibrium partial pressures of all the gaseous species in [5.3], [5.5], [5.7] and [5.8] are obtained within[22,23]. The condition is met provided the surface area of the condensed phase (ZnS here) is large compared with the cross-sectional area of the channel and that unfavourable surface kinetic effects do not intervene[23]. Unfavourable surface kinetics may arise from (i) physical effects, e.g. a surface film of oxide may form on a liquid metal so hindering its vaporisation or (ii) structural effects, e.g. the vaporisation coefficient for phosphorus (red) is exceptionally small ($\simeq 10^{-8}$) due to the structural reorganization in the solid → gas phase transition[24,25]. Liquids, most metals, and isotropically bonded solids have vaporisation coefficients close to unity[26]. Kinetic inhibition for zinc sulphide transport in hydrogen chloride reaction

[5.7] at low partial pressures of HCl has been suggested[27,28]. The experiments which prompted this suggestion were in a closed tube reactor for which the diffusive resistance is five times smaller than in the MEM experiments. The equilibrium assumption is usually verified experimentally, as in this work, by conducting experiments with capsules having different channel dimensions and showing the results are self-consistent.

To derive expressions for the partial pressures of the gaseous species in four equations already mentioned, three coupling parameters (β', ∂, and θ) must be defined. These are

$$\beta' = \frac{j(Zn_2Cl_4)}{j(ZnCl_2)} \; ; \quad \partial = \frac{j(Zn)}{j(S_2)} \; ; \quad \theta = \frac{j(H_2)}{j(H_2S)} \qquad (5.5.1)$$

where j is the flux of the species in the channel and the coupling parameters may be solved from ancillary thermodynamic data on [5.8], [5.3] and [5.5]. Hence an expression for the equilibrium of zinc sulphide transported by hydrogen chloride becomes

$$K_6 = \frac{x^2(2.2)^2(\theta+1)}{D_{(ZnCl_2)}D_{(H_2S)}\Gamma^2(1+2\beta')y^2} \qquad (5.5.2)$$

where $x = \dfrac{\mathring{\omega}RT\ell}{AM_{ZnS}}$,

$$y = \epsilon p - \frac{2x(\partial-2)(\theta+1)}{D_{HCl}\Gamma} ,$$

$$\Gamma = \partial-2\theta-2 \text{ and } \epsilon = \frac{p_{HCl}}{p_{Ar}+p_{HCl}}$$

Full derivation and definition of terms are given in Appendix A2.4.

As more than two gaseous components are present in the channel at any time the effects of multicomponent diffusion (see section 3.4) are taken into account, so D_i in (5.5.2) are multicomponent diffusion coefficients.

As already mentioned to describe this equilibrium system of zinc sulphide transported in hydrogen chloride, the "ZnS/HCl" MEM experimental results ($\mathring{\omega}$) require to be coupled to reliable ancillary thermodynamical data to calculate the coupling flux parameters β', ∂ and θ. These include the vaporisation of zinc chloride (β'), sublimation of zinc sulphide (∂) and the "equilibrium formation" of hydrogen sulphide from its gaseous elements (θ).

Zinc chloride vaporisation has been studied by MEM in chapter 4 and the results interpreted in terms of monomeric and dimeric species in the vapour. The free energy expression (5.5.3) of zinc chloride was derived.

$\Delta G^{O}_{8}/J\ mol^{-1} = -(162.000 \pm 8000) + (202 \pm 11)T$ [640-980 K] (5.5.3)

This equation was used to obtain β' (see table 4.6). Although the temperature ranges of the zinc chloride work and the (ZnS/HCl) studies are not coincident, the zinc chloride dimer makes little contribution to the table 5.7 transport above 1000 K (see table 5.7 for values of β and partial pressures), so this non-coincidence is not a source of serious error. The dissociative sublimation of sphalerite by modified entrainment (equation [5.3] has also been previously described in section 5.4 and equation (5.5.4) obtained was

$\Delta G^{O}_{3}/J\ mol^{-1}\ (374200 \pm 1200) - (190.4 \pm 1.1)T$ [1010-1270 K] (5.5.4)

The results from the MEM experiments with different channel sizes were first processed separately yielding two regression lines in the form $\Delta G^{O}_{7} = a - bT$. Analysis of covariance showed there was no significant probability that the input data arose from different populations; this test confirms that equilibrium partial pressures were obtained within the capsules. The results (145 data pairs, $\mathring{\omega}(T)$, see Appendix A4.5) from the two different capsules and

Table 5.7 Typical values of Coupling Parameters and Equilibrium Partial Pressures (p_i^o/Nm^{-2}) in ZnS(c) + HCl(g) at 1024-1252 K

T/K	$10^5\beta'$	θ	$10^4\partial$	$p^o(ZnCl_2)$	$p^o(Zn_2Cl_4)$	$p^o(HCl)$	$p^o(H_2)$	$p^o(Zn)$	$p^o(S_2)$	$p^o(H_2S)$
1024	1.14	1.28	0.3	359	.0066	5750	29	.002	106	101
1159	0.28	2.60	11.5	800	.0035	5180	84	.222	307	145
1252	0.12	4.03	97.8	1182	.0022	4700	139	3.070	508	154

coupling parameters $\beta' = \frac{j(Zn_2Cl_4)}{j(ZnCl_2)}$; $\partial = \frac{j(Zn)}{j(S_2)}$; $\theta = \frac{j(H_2)}{j(H_2S)}$

four different HCl doping levels were then pooled and equation (5.5.5.) obtained by regression to give

$$\Delta G^{\circ}_{7}/\text{J mol}^{-1} = (95060 \pm 2700) - (38.7 \pm 2.4)T \quad \langle 1140\ \text{K}\rangle \quad [1023\text{-}1263\ \text{K}] \qquad (5.5.5)$$

the free energy equation of zinc sulphide transport in hydrogen chloride. The uncertainty intervals are the standard deviations of the regression coefficient.

A Free Energy Equation for the corresponding equilibrium [5.6] involving liquid Zinc Chloride instead of gaseous Zinc Chloride in equilibrium [5.7]

The equilibrium of central importance to this study is equation [5.6]. The coefficients of the experimentally determined equation (5.5.5) were scaled to refer to 808 K (the mean temperature of the $ZnCl_2$ vaporisation study, see below) using C_p results for HCl and H_2S from JANAF tables [12], for $ZnCl_2(g)$ from Givan and Loewenschuss[29] and for $ZnS(\beta)$ from Pankratz and King[16] and Stuve[15]. Hence our experimental reaction (ZnS/HCl) equation [5.7] now scaled from <1140 K> to <808 K> becomes

$$\Delta G^{\circ}_{7}/\text{J mol}^{-1} = (98260 \pm 2700) - (42.0 \pm 2.4)T \quad \langle 808\ \text{K}\rangle \qquad (5.5.6)$$

The zinc chloride vaporisation study by MEM in the range 638 to 978 K described in chapter 4 for range 638 to 978 K

$$ZnCl_2(l) = ZnCl_2(g) \quad [5.9] \; [638\text{-}978\ K] \quad (5.5.7)$$

gave

$$\Delta G^{o}_{9}/J\ mol^{-1} = (126600 \pm 500) - (127.6 \pm 0.5)T \quad (5.5.8)$$

Subtracting equation (5.5.8) from equation (5.5.6) yields the free energy equation for equilibrium [5.6] involving liquid zinc chloride,

$$\Delta G^{o}_{6}/J\ mol^{-1} = (-28340 \pm 2800) + (85.6 \pm 2.4)T \quad <808\ K> \quad (5.5.9)$$

which is valid over a temperature range of 638-978 K, this being within the liquid region of $ZnCl_2$ (591-1005 K). Equilibrium constants calculated from this equation (5.5.9) are compared in table 5.8 with the two isolated literature results of Britske and Kapustinskii[30].

Table 5.8 Comparison of K_6 calculated from equation (5.5.9) with literature results

$ZnC(c,\beta) + 2HCl(g) = ZnCl_2(l) + H_2S(g)$ [5.6] K_6 (5.5.9)

	K_6(565 K)	K_6(635 K)
Britske[30]	0.072	0.021
This Work	0.014±0.008	0.007 ±0.004

Although the proportional error in K_6 is ca. 60%, the values are significantly different from those of Britske and Kapustinskii[30].

Third and Second Law Analysis on Zinc Sulphide Transported in Hydrogen Chloride

The free energy values for equation [5.7] were analysed by the third law method. These free energy functions were taken from the literature [12,15,16,29]. Using values of $(H^{o}_{1143} - H^{o}_{298})$ from these same sources, the corresponding second law estimates of ΔH^{o}_{298} were obtained from ΔH^{o}_{7} (1143 K) = 95.1±2.7 kJ mol^{-1} extracted from equation (5.5.5), the experimental result of (ZnS/HCl), and method illustrated in tables 5.4 and 5.5. The contribution of ΔH^{o}_{7} from the $T\Delta(fef)$ term in the third law analysis is ca. 50% and the coincidence between the second and third law results suggests the free energy functions for the components in equation [5.7] are in good order as shown in table 5.9.

Table 5.9 Second and Third Law Analysis of

$ZnS(\beta,c) + 2HCl(g) = ZnCl_2(g) + H_2S(g)$

K_7, ΔH°_7 <298 K> [5.7]

	ΔH°_7 (298 K)/kJ mol^{-1}
Second Law	103.9±5.4
Third Law	100.8±0.4

Uncertainty intervals are ±2 (standard deviations of the Mean)

5.6 Conclusion

The principal conclusion from this work is that the transition $ZnS(\beta) \rightarrow ZnS(\alpha)$ is nearly athermal, both at the transition temperature and at 298 K. This is in agreement with the BM results [15,16] but at variance with Kapustinskii and Chenkova's solution calorimetric study[31]. Briefly, this Russian work consisted of measuring the enthalpies of reaction of the α- and β-phases in concentrated HCl using an adiabatic calorimeter at 293 K. With the same final thermodynamic state in each case, the difference in the heat of reaction is equal to the heat of transition. The solution of the β-phase was so sluggish that the experiments were truncated when dissolution was ca. 90% complete, the extent of reaction being determined by analysis. The uncertainty attendant on solution calorimetry with slow reactions is well-established[32] and the truncation procedure must be regarded as of doubtful validity. Further, when this work was repeated by the BM group[33] it was the β-phase that proved more difficult to dissolve and no results were reported for it. The BM result for the α-phase by reaction calorimetry is ΔH_f° [ZnS,α]298 = -191.9±0.8 kJ mol^{-1} which differs by 4.4 kJ mol^{-1} from our third law result.

The transport of zinc sulphide in hydrogen chloride has been investigated by modified entrainment. Combining these results with the results from the vaporisation study of $ZnCl_2$ in Chapter 4 the corresponding "liquid" reaction [5.6] has been derived. It is this reaction that has been proposed as a procedure to remove ZnS contamination in a zinc chloride hydrocracking melt[34].

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Chapter 6

Thermodynamics of Dissociation of Diamminedichlorozinc(II) ($ZnCl_2(NH_3)_2$)

6.1 Introduction

Molten zinc chloride has been proposed as a hydrocracking solvent for coal slurries and heavy oil fractions[1,2]. Nitrogen is one several heteroatoms inevitably introduced with the feedstock and is reduced to ammonia (NH_3) under the usual operating condition of 420°C and 170 atm. of hydrogen. The NH_3 forms strong complexes, principally $ZnCl_2NH_4Cl$, $ZnCl_2(NH_3)_2$ and $ZnCl_2NH_3$, with zinc chloride and these steadily accumulate in the melt[2,3]. As part of the programme to study the thermodynamics of reactions involving molten zinc chloride and its regeneration from contaminated melts, the thermal decomposition of $ZnCl_2(NH_3)_2$ has been examined by modified entrainment.

6.2 Materials

Diamminedichlorozinc(II) was made by the method of Perchard and Novak[4] from ethanolic zinc chloride into which ammonia was passed. The agreement between the calculated and experimental analysis results was shown to be satisfactory in section 2.10.

6.3 Experimental

Diamminedichlorozinc(II) crystals were observed to melt with decomposition in an open m.p. tube at a temperature range from 190 to 250°C (details are given below).

The MEM transport of $ZnCl_2(NH_3)_2$ in argon was studied in the temperature range from 166 to 399°C. Forty-five measurements were recorded with approximately 1 mg mass loss per point, the total initial mass being 231.4 mg; the rates of mass loss $\mathring{\omega}(T)$ varied from 2×10^{-10} kg s^{-1} to 4×10^{-12} kg s^{-1} dependent upon the temperature of the sample and duration of time held at that particular temperature. The experimental MEM data on $ZnCl_2(NH_3)_2$ are collected in Appendix A4.6.

6.4 Results

The following phase changes of diamminedichlorozinc(II) were noted while heating a sample in a melting point tube:

i) perceptible softening in region 190 to 220°C, however 90+% was still solid. A possible reaction is

$$\underset{A}{ZnCl_2(NH_3)_2(c)} = \underset{B}{ZnCl_2NH_3(\ell)} + NH_3(g) \qquad [K_3],[\Delta G_1^\circ] \qquad (6.4.1)$$

(B "wets" A making it look soft),

ii) at 240°C, only 70% was solid,

iii) 243°C, only 50% was solid and at

iv) 249 to 252°C rapid melting with gas evolution.

During the MEM experiments it was found that only at temperatures below 228^oC were reproducible values of $\mathring{\omega}$ obtained. Furthermore a plot of ln$\mathring{\omega}$ vs. $^1/_T$ was nearly linear in the range 166 to 228^oC. At higher temperatures values of $\mathring{\omega}$ were time-dependent and irreproducible - see figure 6.1 where the experimental sequence is noted.

6.5 Discussion

Stoichiometry of the Thermal Decomposition

Zinc Chloride forms several ammines, $ZnCl_2(NH_3)_n$, where n = 6, 4, 2, 1.5, 1, 0.5 and 0.167. Their thermal stability and phase interrelationships have been well-documented[3,5,11]. The monoammine and the diammine have been most thoroughly characterized, viz. by X-ray diffraction[12], vibrational spectroscopy[4], temperature dependence of viscosity and conductivity[8], thermogravimetric[5,6] and thermomechanical analysis[5] and molecular mass in solution [8]. As mentioned in Section 6.4, the starting material in this work, $ZnCl_2(NH_3)_2$ remains solid on heating to over 190^oC when the presence of a liquid phase ($ZnCl_2NH_3$, see below) becomes apparent. Quantitative analysis[9] of all of the phases present in a closed system between 220^o to 540^oC and initially charged with diammine suggest the equilibrium stoichiometry as $ZnCl_2(NH_3)_2 = ZnCl_2NH_3 + NH_3$. Furthermore the product of the

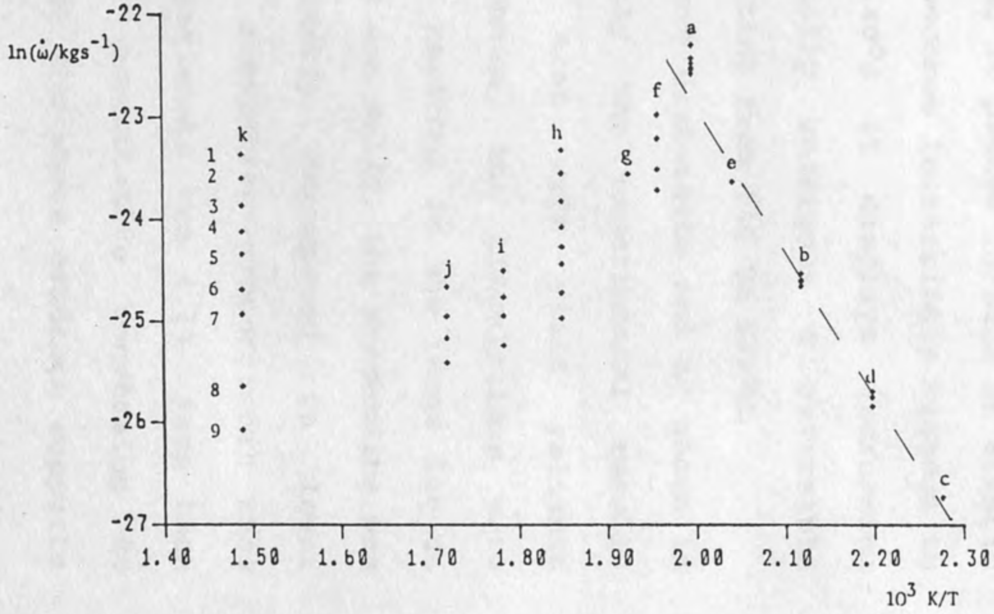
Figure 6.1 Evaporation of Diamminedichlorozinc(II)

Temperature Range [439-672 K]

Initial Mass of Sample $ZnCl_2(NH_3)_2$ = 231.4 mg

Possible equilibria and mass loss (Δm) corresponding to completion of each reaction

		Δm/mg
$ZnCl_2(NH_3)_2$ ->	$ZnCl_2(NH_3)_{1.5}(\ell) + 0.5NH_3(g)$	11.6
	$ZnCl_2\ NH_3(\ell) + NH_3(g)$	23.1
	$ZnCl_2(c) + 2NH_3(g)$	46.3



Chronological Sequence	T/K	Kinetic Inhibition*	Cumulative Mass Loss
a	501	?	-
b	472	x	-
c	439	x	-
d	455	x	-
e	490	x	-
f	511	✓	f1 9.4
g	520	✓	g1 14.3
h	541	✓	h9 21.5
i	561	✓	i4 24.7
j	582	✓	
k	672	✓	k9 38.7

* Kinetic inhibition of sample causes $\dot{\omega}$ to be irreproducible with time e.g. k1 = 7.1×10^{-11} kg s^{-1} to k9 = 0.5×10^{-11} kg s^{-1}.

reaction under investigation, $ZnCl_2NH_3$, may be prepared by the controlled thermal decomposition[5,8] of the diammine in an open system at 200°C until the proportional mass loss is 10%. The thermal stability of $ZnCl_2NH_3$ has been examined in open systems by Zubakhina[6] and Volova et al[5] who reported insignificant decomposition to $ZnCl_2(NH)_3)_n$ where $n < 1$ below 320°C and 380°C respectively.

The physical properties of monoaminedichlorozinc $ZnCl_2NH_3$ have been extensively studied[5,8]. The room temperature phase is a glassy polymer, $(ZnCl_2NH_3)_m$ where $m \simeq 30$. On heating it passes through an elastic phase (34 to 60°C) and becomes increasingly viscous to 90°C. From 90 to 140°C it displays increasing crystallinity, and finally undergoes a reversible depolymerization and melting from 140 to 148°C.

Clearly from the above discussion and as shown in figure 6.1, it is only the experimental results obtained below 228°C that will yield reliable thermodynamic data. Hence, the calculations were confined to 11 raw data readings in the range 166 to 228°C where the diammine was solid, the monoammine was liquid and insignificantly decomposed to lower ammines. Further the cumulative proportional mass loss throughout the experiments was 4.1%, less than the 10% required for quantitative conversion to $ZnCl_2NH_3$. Taken together the above evidence supports a reaction stoichiometry given by equation (6.4.1) i.e. the conversion of the solid diammine to form liquid monoammine with the liberation of ammonia.

Modified Entrainment

For equilibrium (6.4.1), involving a single gaseous species, the partial pressure of NH_3($p^o_{NH_3}$ is given by

$$p^o_{NH_3} = P(1 - e^{-\xi}) \qquad (6.5.1)$$

where $\xi = \mathring{\omega}RT\ell/DAMP$. $\xi = \mathring{\omega}RT\ell/DAMP$. $\mathring{\omega}$ is the rate of mass loss at temperature T, ℓ/A is the length over the cross-sectional area of the capsule capillary (2.006 x 10^4 m^{-1}), M is the molecular mass of NH_3, P is the total system pressure (usually a few mmHg above atmospheric pressure) and *D* is the binary diffusivity of NH_3 in Ar, see Appendeces A2.5, A3.9 and A4.6 for further ancillary information on the diammine. The diffusivity was estimated over the experimental temperature range (438 to 503 K) from the Lennard-Jones potential parameters for NH_3 and Ar[13]

$$D(NH_3,Ar)/m^2s^{-1} = 1.825 \times 10^{-5}\ (T/273.15)^{1.842}$$

$$[438\text{-}503\ K] \qquad (6.5.2)$$

Only limited experimental evidence[14] exists for this system and not within our temperature range. The equilibrium constant for reaction (6.4.1), $p^{o}_{NH_3}/p^{\theta}$, (p^{θ} = 101325 Nm^{-2}) was formed from equations (6.5.1) and (6.5.2) and the corresponding ΔG^{o}_{1} was linearly regressed against T/K to give equation (6.5.3) for the thermal decomposition of the diammine complex

$$\Delta G^{o}_{1}/J\ mol^{-1} = (118500 \pm 3800) - (218 \pm 8)T \qquad [439\text{-}510\ K] \quad (6.5.3)$$

The uncertainty intervals in equation (6.5.3) are standard deviations of the regression coefficients. The dissociation pressure above $ZnCl_2(NH_3)_2$(crystal) has been reported before[15,16] at five temperatures in the range 401 to 490 K. The decomposition reaction was quoted as equation (6.4.1) except that the monoammine phase was written as solid. Converting these early results to free energies we obtain

$$\Delta G^{o}/J\ mol^{-1} = (118800 \pm 9600) - (219 \pm 21)T \qquad [401\text{-}490\ K] \quad (6.5.4)$$

The coefficients in equation (6.5.4) have larger uncertainty intervals but are close to those of equation (6.5.3).

6.6 Conclusion

The Gibb's free energy equation (6.5.3) for the conversion of diamminedichlorozinc(II) in the temperature range [439 to 501 K] has been derived using the modified entrainment method and compares favourably with that of earlier workers[15,16] except they failed to identify the monoammine phase as liquid. On further heating, the sample develops a viscous surface film which hinders the rate of weight loss subsequently as shown in figure 6.1. This suggests the system has become kinetically rather than thermodynamically controlled and hence no thermodynamic data (Gibbs' free energy equations) may be derived because the system is no longer at equilibrium.

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Appendix 1

Calibration of Thermocouples and Temperature Profiles of Furnaces Used in the MEM Experiments

A1.1 Calibration of Thermocouples

Figure A1 shows that the Keithley Tc type K is in satifactory agreement with the mercury-in-glass thermometer (exposed stem-end correction applied) to within experimental error of ± 2°C.

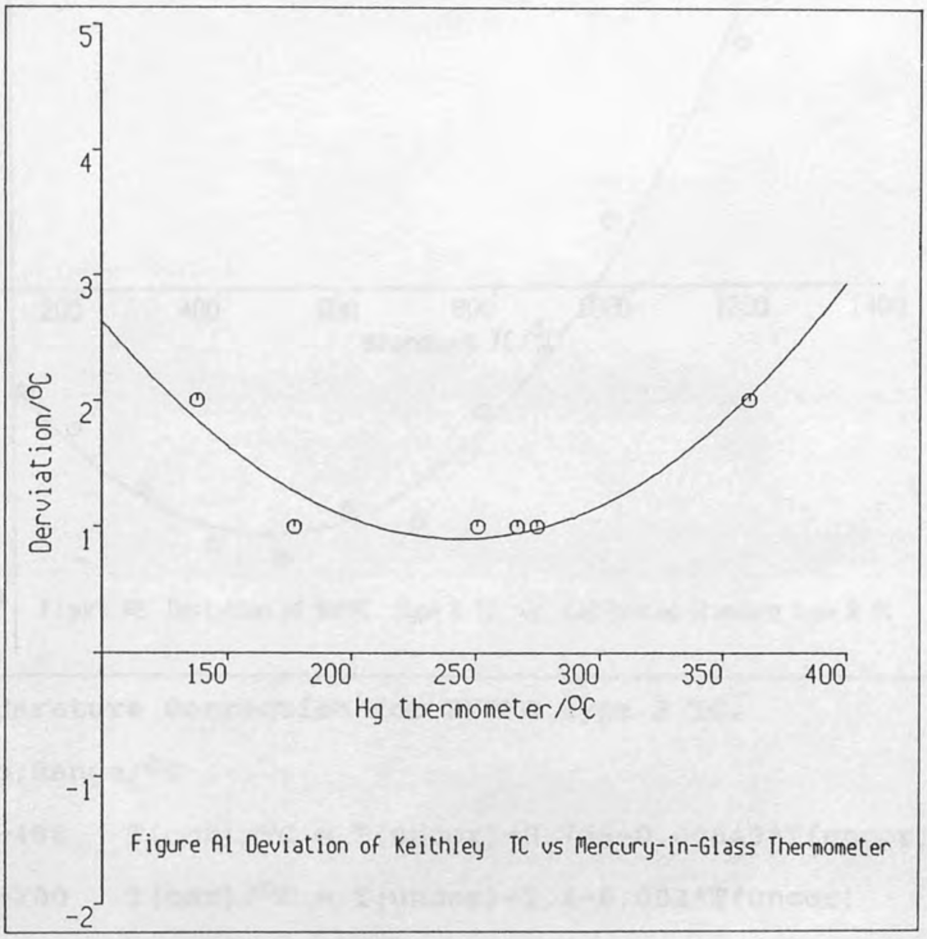

Figure A1 Deviation of Keithley TC vs Mercury-in-Glass Thermometer

Equilibrium systems studied using type K Tc were Hg in inert gases, temperature range [148-317°C] and $ZnCl_2 2NH_3$ in argon, temperature range [166-399°C].

Figure A2 shows there is a slight deviation in the temperature readings between RHBNC type R TC and the calibrated standard type R TC. Consequently a series of temperature corrections were applied to the following systems

Zn in inert gases [417-867°C] $ZnCl_2$ in Ar [365-705°C]

ZnS in H_2 [737-1172°C] ZnS in HCl [750-990°C].

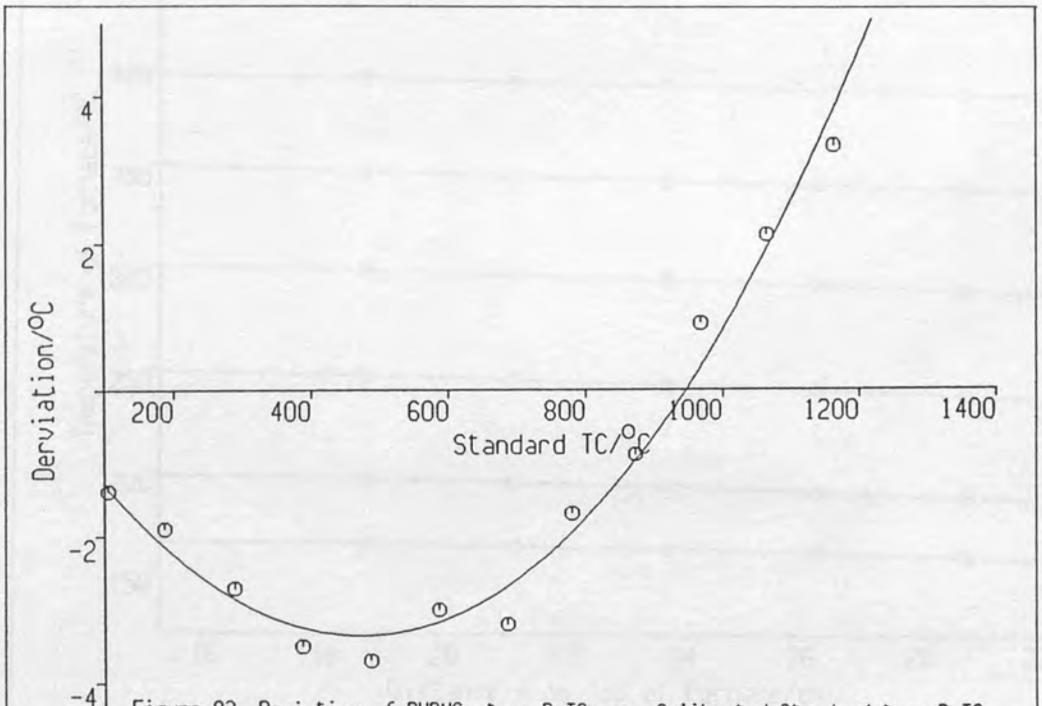

Figure A2 Deviation of RHBNC type R TC vs Calibrated Standard type R TC

Temperature Correction for RHBNC type R TC.

Temp.Range/°C

107-488 T(cor)/°C = T(uncor)-0.759-0.00643*T(uncor)

350-700 T(cor)/°C = T(uncor)-2.4-0.002*T(uncor)

489-586 T(cor)/°C = T(uncor)-3.6

587-1162 T(cor)/°C = T(uncor)-10.9+0.012*T(uncor)

cor = corrected temp. uncor = uncorrected temp.

A1.2 Furnace Profiles used in MEM Studies

Type 1: Gold Furnace 170-450°C

Systems studied with Gold Furnace with insulation lagging were Hg in inert (non-reacting) gases (148-317°C) and $ZnCl_2(NH_3)_2$ in argon (166-399°C).

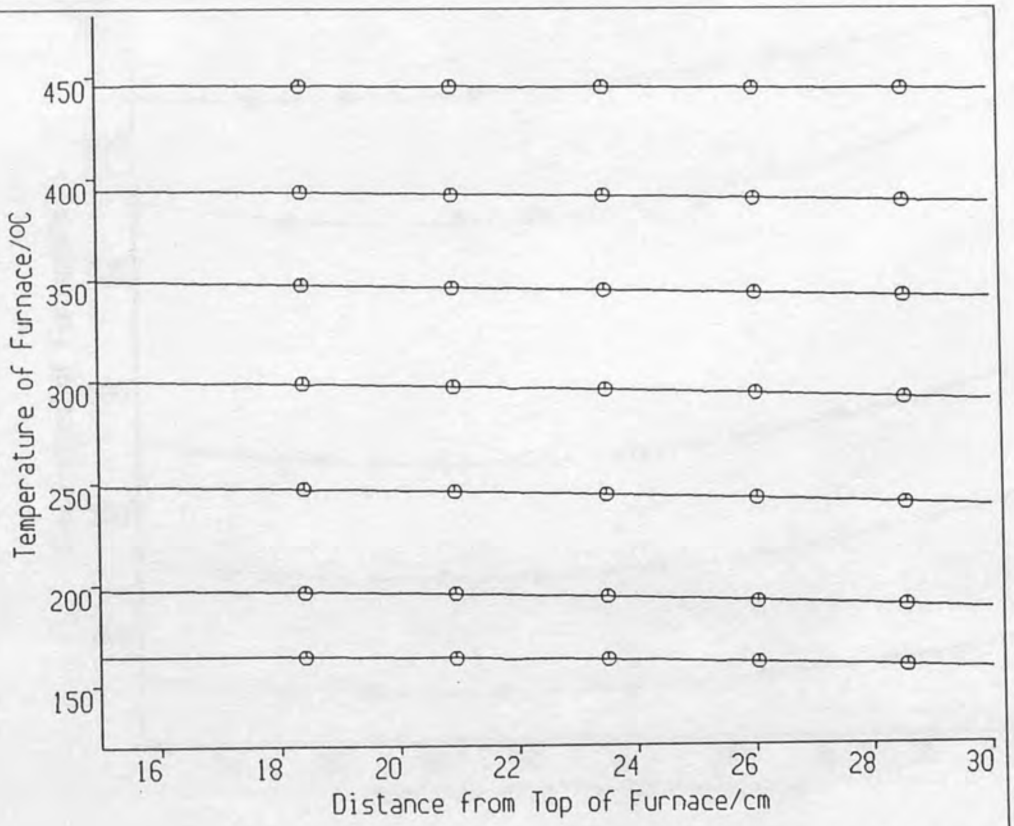

Figure A3 Temperature Profiles of Gold Furnace
Set Temperature Range 170°C to 450°C

Technical Specification of Gold Furnace:

40 mm Temp Plateau ± 2°C in all cases ^{18} region ^{24}.

Cylindrical shaped ceramic wool lagging ^{33} region ^{51}.

Downward argon flow at 90 cm^3 min^{-1} (stp).

Control Tc positioned at 21 cm, between furnace tube and silica tube of MEM rig. Measuring Tc used - type K.

Type 2: Demountable Furnace 400-900^{o}C

Systems studied with Demountable Furnace and one layer of insulation were Zinc in inert gases (455-862^{o}C) and Zinc Chloride in argon (365-705^{o}C).

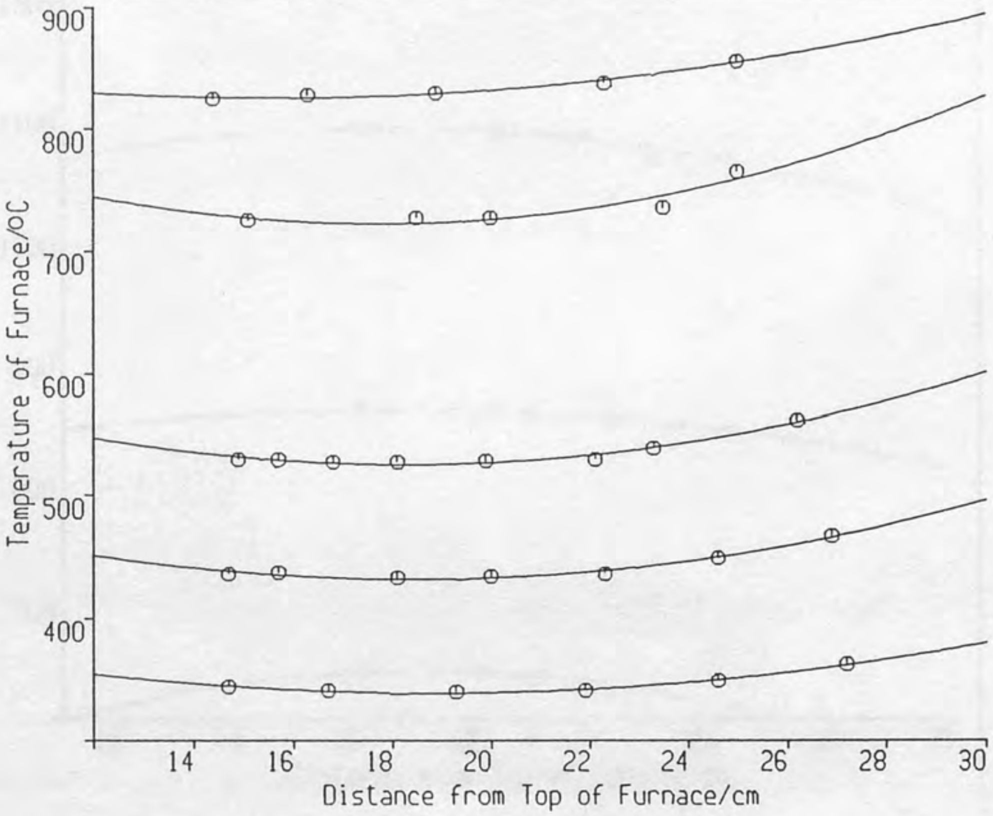

Figure A4 Temperature Profiles of Demountable Tube Furnace Set Temperature Range 400°C to 900°C

Technical Specification of Demountable Furnace:

40 mm Temp Plateau ± 2^{o}C in all cases ^{17} region ^{21}.

One layer of ceramic wool insulation ^{28} region ^{45}.

Downward nitrogen flow at 90 cm^{3} min^{-1} (stp).

Control Tc positioned at 34 cm between insulator and outer furnace wall. Measuring Tc (RHBNC) type R.

Type 3: Demountable Furnace 600-1200°C

Systems studied with Demountable Furnace with two layers of insulation were zinc sulphide in hydrogen (737-1172°C) and zinc sulphide in hydrogen chloride (750-990°C).

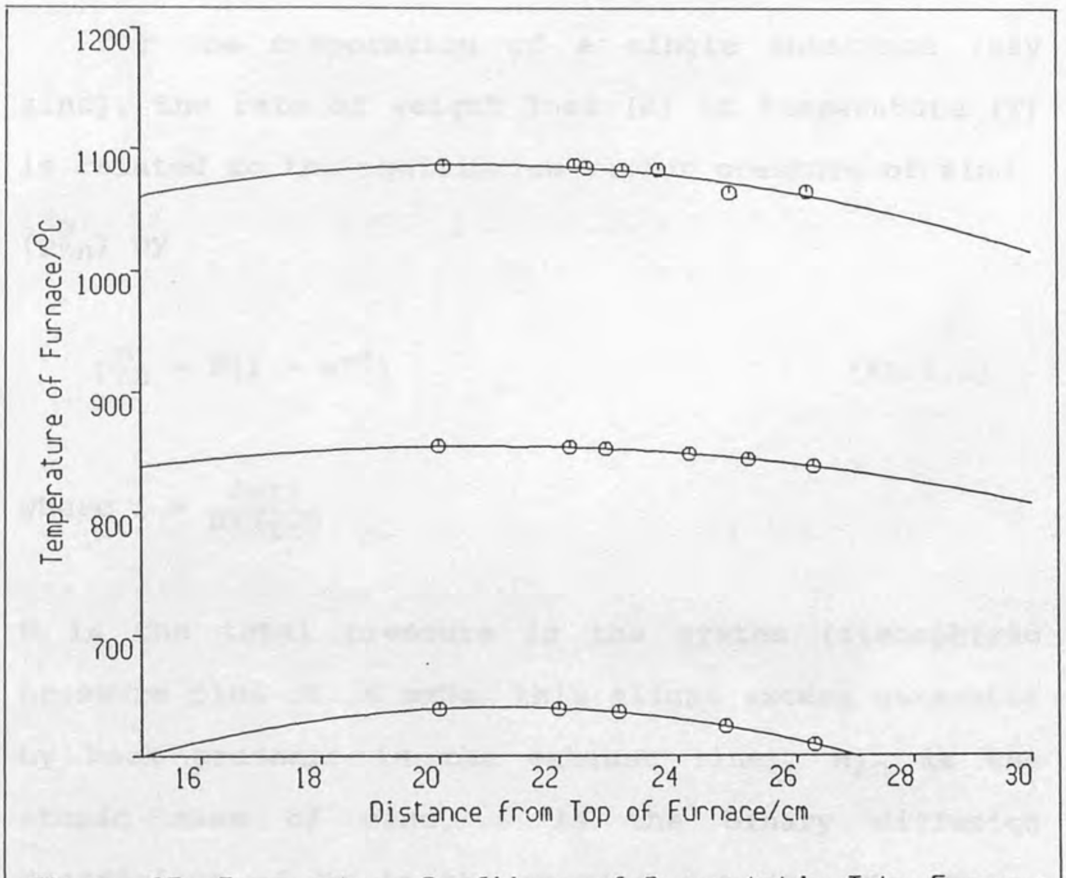

Figure A5 Temperature Profiles of Demountable Tube Furnace
Set Temperature Range 600°C to 1200°C

Technical specification of Demountable Furnace:

40 mm Temp Plateau ± 2°C in all cases ^{19} region ^{23}.

2 layers of c. wool insul^{n} ^{0} region ^{45} ^{33} region ^{45}.

Downward nitrogen flow at 90 cm^{3} min^{-1} (stp).

Control Tc positioned at 34 cm between insulator and outer furnace wall. Measuring Tc (RHBNC) type R.

Appendix 2
MEM Transport Equations

A2.1 Evaporation of a Single Substance (Zn,Hg) in inert gases (H_2, He, N_2, Ar)

Relevant Programs: ZINCW.FOR and MERCURYW.FOR

For the evaporation of a single substance (say zinc), the rate of weight loss ($\mathring{\omega}$) at temperature (T) is related to the equilibrium vapour pressure of zinc (p^o_{Zn}) by

$$p^o_{Zn} = P(1 - e^{-\xi}) \qquad \text{(A2.1.1)}$$

where $\xi = \dfrac{\mathring{\omega}RT\ell}{DAM_{Zn}P}$

P is the total pressure in the system (atmospheric pressure plus ca. 4 mmHg, this slight excess generated by back pressure in the exhaust line), M_{Zn} is the atomic mass of zinc, D is the binary diffusion coefficient of Zn in the carrier gas (H_2, He, N_2 or Ar), ℓ and A are the length and cross-sectional area of the channel.

The algebraic equation (A2.1.1) and derivation of binary diffusion coefficients have been discussed in sections 1.4 and 3.5 of this thesis. When the partial pressure of the substance is known, then the binary diffusion coefficients may be calculated as a function of temperature.

A2.2 $ZnCl_2$ Transport in Argon

Equilibria considered to be monomer and dimer zinc chloride composition only

$$ZnCl_2(l) = ZnCl_2(g) \qquad K_1$$
$$2ZnCl_2(g) = Zn_2Cl_4(g) \qquad K_2$$

To set up flux equations, the following notation is used $1 \equiv ZnCl_2$ and $2 \equiv Zn_2Cl_4$

$$\text{Zn flux } j_{Zn} = j_1 + 2j_2$$
$$\text{Cl flux } j_{Cl} = 2j_1 + 4j_2$$

Define coupling flux parameter, α, as the flux ratio for the monomer and dimer as

$$\alpha = \frac{j_1}{j_2}$$

then total flux of system, J, may be rewritten in terms of the coupling parameter α

$$J = j_1 + j_2 = j_1\left[\frac{\alpha+1}{\alpha}\right]$$

The experimentally measured (or emergent) flux from the channel j_e

$$j_e = j_{Zn} = j_1 + 2j_2 = j_1 \left[\frac{\alpha+2}{\alpha}\right] = \frac{\mathring{\omega}}{AM_{ZnCl_2}}$$

Expression for j_i/J

$$\frac{j_1}{J} = \frac{\alpha}{\alpha+1} \quad ; \quad \frac{j_2}{J} = \frac{1}{\alpha+1} \quad ; \quad \frac{j_e}{J} = \frac{\alpha+2}{\alpha+1}$$

Partial pressures of zinc chloride monomer and dimer

In general $$\frac{p_i^a}{P} = \frac{j_i}{J} + \left\{\frac{p_i^b}{P} - \frac{j_i}{J}\right\} e^{-\xi_i} \qquad \text{(A2.2.1)}$$

where $\xi_i = \dfrac{JRT\ell}{PD_i}$ capillary channel $\left|\left|\begin{matrix} b \\ \\ a \end{matrix}\right|\right|$

$$= \frac{j_e RT\ell}{PD_i} * \frac{J}{j_e} = \frac{\mathring{\omega} RT\ell}{D_i AM_1 P}$$

when $\dfrac{p_i^b}{P} \approx 0$, $\dfrac{p_i^a}{P} = \dfrac{j_i}{J}(1 - e^{-\xi_i})$

and when $\xi_i << 1$, $$\frac{p_i^a}{P} = \frac{j_i}{J}\xi_i \, . \qquad \text{(A2.2.2)}$$

Then $$\xi_1 = \frac{\mathring{\omega} RT\ell}{D_1 AM_1 P}\left\{\frac{\alpha+1}{\alpha+2}\right\}$$

and $$\xi_2 = \frac{\mathring{\omega} RT\ell}{D_2 AM_1 P}\left\{\frac{\alpha+1}{\alpha+2}\right\}$$ Notice M_1 in denominator not M_2 in this expression

$\therefore$ Partial Pressures $p_1 = \frac{\alpha}{\alpha+2} \cdot \frac{x}{D_1}$ and $p_2 = \frac{1}{\alpha+2} \cdot \frac{x}{D_2}$

where $x = \frac{\mathring{\omega} RT\ell}{AM_1}$

Expression for equilibrium constants K_i becomes

$$K_1 = \frac{p_1}{p^\theta a_{ZnCl_2(l)}} = \frac{p_1}{p^\theta} = \frac{\alpha}{\alpha+2} \cdot \frac{\alpha}{D_1 p^\theta} \qquad (A2.2.3)$$

$$K_2 = \frac{p_2 p^\theta}{(p_1)^2} = \frac{(\alpha+2)}{\alpha^2} \cdot \frac{D_1^2\, p^\theta}{D_2\, x} \qquad (A2.2.4)$$

These two equations (A2.2.3) and (A2.2.4) may be solved simultaneously to find x (and hence $\mathring{\omega}$), the master equation:

$$\mathring{\omega}_{ZnCl_2} = \frac{AM_1}{RT\ell} \left\{ K_1 D_1 p^\theta + 2K_1 K_2 D_2 p^\theta \right\} \qquad (A2.2.5)$$

MEM transport of $ZnCl_2$ with Monomer Species consideration Only

Relevant computer program: ZNCL2HT.FOR

When the dimer concentration of the evaporation of zinc chloride is considered negligible, the MEM algebraic expressions are similar as those derived for zinc or mercury in Appendix A2.1. As before

$$ZnCl_2(l) \quad = \quad ZnCl_2(g) \qquad\qquad K_1$$

$$K_1 \quad = \quad \frac{p_1}{p^{\theta}} \quad \text{assuming the activity of molten } ZnCl_2 \text{ to be unity}$$

where $p_1 \quad = \quad P(1 - e^{-\xi_1})$ and $\xi_1 \quad = \quad \frac{\mathring{\omega}_1 RT\ell}{D_1 AM_1 P}$

Avoiding the Transport Function (ξ) Approximation
Relevant Computer Program: ZNCL2K2.FOR

For practical MEM algebraic simplicity the expansion of the transport function (ξ) is usually

$(1 - e^{-\xi}) \simeq \xi$ where $\xi \ll 1$

when several heterogenous reactions are taken into consideration. For greater accuracy in experiment results the exact formulae for the zinc chloride transport may be used. The monomer thermodynamic constants are determined by using the negligible dimer concentration assumption. This concept being developed earlier in program ZNCL2HT.FOR, and in Chapter 4, is then reprocessed at a much lower or higher temperature where dimer concentration is significant.

The monomer and dimer partial pressures are as before

$$p_1 = \frac{\alpha}{\alpha+1}P(1 - e^{-\xi_1}) \quad ; \quad \xi_1 = \frac{\mathring{\omega}RT\ell}{D_1AM_1P}\left[\frac{\alpha+1}{\alpha+2}\right] \qquad (A2.2.6)$$

$$p_2 = \frac{1}{\alpha+1}P(1 - e^{-\xi_2}) \quad ; \quad \xi_2 = \frac{\mathring{\omega}RT\ell}{D_2AM_1P}\left[\frac{\alpha+1}{\alpha+2}\right] \qquad (A2.2.7)$$

Redefining the equilibrium constant K_1 and the experimental data by

letting $A = \frac{K_1p^\theta}{P}$ and $B = \frac{\mathring{\omega}RT\ell}{D_1AMP}$

then $A = \frac{\alpha}{\alpha+1}\left\{1 - \exp\left[- B\left[\frac{\alpha+1}{\alpha+2}\right]\right]\right\}$

and truncating the above expression to the power of 2

$$A = \frac{\alpha}{\alpha+1}\left[B\left[\frac{\alpha+1}{\alpha+2}\right] - \frac{1}{2}B^2\frac{(\alpha+1)^2}{(\alpha+2)^2}\right]$$

A quadratic equation for α is thus derived by expansion of the above equation

$$\alpha^2(2A - 2B + B^2) + \alpha(8A - 4B + B^2) + 8A = 0$$

The flux parameter α may now be calculated from the knowledge of the monomer equilibrium (K_1) using program ZNCL2HT.FOR and experimental data $\mathring{\omega}(T)$. Hence substitution of α into equation (A2.2.7), the dimer equilibrium may be extracted at the appropriate temperature where dimer concentration is significant.

MEM transport of $ZnCl_2$ coupled to Ancillary Vapour Pressure Data obtained from the Literature

Relevant computer program: ZnCL2PG.FOR

The master equation (A2.2.5) of zinc chloride may be recast in terms of monomer (p_1) and dimer (p_2) partial pressures by substituting them in place of the equilibrium constants K_1 and K_2.

$$\mathring{\omega} = \frac{AM_1}{RT\ell}[D_1p_1 + 2D_2p_2] \qquad \text{(A2.2.8)}$$

Using ancillary absolute vapour pressure measurements ($P_T = p_1 + p_2$) of zinc chloride, gives p_1 and p_2 separately over the common temperature range. The enthalpy and entropy values for the monomer and dimer may be extracted by standard linear regression procedures.

A2.3 "Congruent" sublimation of ZnS in Hydrogen

Relevant Computer Program: ZNSDS3G.FOR

The ZnS transport was performed in hydrogen giving the participating reactions

$$ZnS(c,\beta) + H_2(g) = Zn(g) + H_2S(g) \qquad K_1 \qquad [5.1]$$

and

$$ZnS(c,\beta) = Zn(g) + \tfrac{1}{2}S_2(g) \qquad K_3 \qquad [5.3]$$

The difference between these two equations is

$$H_2(g) + \tfrac{1}{2}S_2(g) = H_2S(g) \qquad K_5 \qquad [5.5]$$

and it is more convenient when formulating the flux equation to consider [5.3] and [5.5] as the participating reactions since the zinc sulphide entrainment only two of the above equations are independent.

Setting up flux equation for the elements and using the numerical notations 1 ≡ H_2, 2 ≡ H_2S, 3≡ S_2, 4 ≡ Zn and 5 ≡ ZnS.

Zn Flux $\quad j_{Zn} = j_4$

H Flux $\quad j_H = 2j_1 + 2j_2$

S Flux $\quad j_{S_2} = 2j_3 + j_2$

A coupling parameter, ∂, defined as the flux ratio in the capillary of Zn(g) to S_2(g)

$$\partial = \frac{j_4}{j_3}$$

In the absence of hydrogen (say argon), $\partial = 2$ as the sublimation is congruent.

Mass balances of flux equations

$j_1 + j_2 = 0$ (no net flux of H, i.e. no sink)

$$\left.\begin{aligned} j_5 &= j_4 \\ j_5 &= 2j_3 + j_2 \end{aligned}\right\} \therefore j_4 = 2j_3 + j_2 = \frac{2j_4}{\partial} + j_2$$

Writing all the fluxes in terms of j_4

$$j_1 = j_4\left[\frac{2}{\partial} - 1\right],\ j_2 = j_4\left[1 - \frac{2}{\partial}\right]$$

$$j_3 = \frac{j_4}{\partial},\ j_4 = j_4,\ j_5 = j_4 = j_{\text{emergent}}$$

and the sum of all the fluxes becomes

$$J = j_1 + j_2 + j_3 + j_4 = j_4\left[\frac{\partial+1}{\partial}\right]$$

The partial pressures of the system can now be in terms of fluxes and transport expressions. Then by using the transport function approximation the partial pressures of the system may be derived

$$\frac{p_i}{P} = \frac{j_i}{J}\,\xi_i$$

where $$\xi_i = \frac{JRT\ell}{D_iP} = \frac{\mathring{\omega}RT\ell}{D_iAM_5P}\,\frac{J}{j_e}$$

Thus solving the flux equation K_3 and K_5 may be written as functions of $\mathring{\omega}$, ∂, T, diffusion coefficients channel resistance, total pressure and fundamental constants as shown below.

$$K_3 = \left[\frac{\mathring{\omega}RT\ell}{M_5Ap^\theta}\right]^{1\cdot5} / [D_4(D_3\partial)^{0\cdot5}] \qquad \text{(A2.3.1)}$$

$$K_5 = \left[\frac{\mathring{\omega}RT\ell D_3p^\theta}{M_5A\partial}\right]^{0\cdot5}\left[\frac{\partial-2}{PD_2}\right] \qquad \text{(A2.3.2)}$$

The term $\mathring{\omega}$ is readily eliminated from these equations leaving a cubic expression in ∂. Substituting literature values for K_3 and K_5 (see eqn. (5.4.4) and table 5.4), the cubic which has only one real positive root was solved exactly giving $\partial \simeq 10^3$ at 1425 K. Consequently $\partial-2$ was approximated to ∂ in (A2.3.2) and then ∂ is eliminated from (A2.3.1) and (A2.3.2) to give (A2.3.3)

$$K_3 = \left[\frac{\mathring{\omega} RT\ell}{M_5 A}\right]^2 / (D_4 D_2 K_5 p^\theta P) \qquad \text{(A2.3.3)}$$

which is identical to equation (5.4.1). The physical significance of the large values of ∂ is that because equilibrium [5.5] lies to the right in our temperature range, the S_2 is transported mainly as H_2S.

In a system of more than 2 components the effects of multicomponent diffusion must be included. A second order treatment of this effect (see Section 3.4 and relevant computer program in Appendix A3.7) permits the multicomponent diffusion coefficient (D_i) to be written in terms of the corresponding binary diffusion coefficient ($\mathcal{D}_{ij}$) with respect to the majority component (hydrogen).

A2.4 Transport of ZnS with Hydrogen Chloride in Argon

Relevant Computer Program: ZNSHCl10.FOR

The partial pressures of the gaseous species in equations [5.3], [5.5], [5.7] and [5.8] (see Chapter 5) are calculated from the general equation (A2.2.1). As four interdependent equilibria are involved, three coupling parameters (β', ∂ and θ) are defined,

$$\beta' = \frac{j(Zn_2Cl_4)}{j(ZnCl_2)} \; ; \quad \partial = \frac{j(Zn)}{j(S_2)} \; ; \quad \theta = \frac{j(H_2)}{j(H_2S)} \qquad (A2.4.1)$$

where j is the flux of the species in the channel. The net elemental fluxes are written in terms of the fluxes of the participating species e.g.

$$Flux(Zn) = j(ZnCl_2) + 2j(Zn_2Cl_4) + j(Zn) \qquad (A2.4.2)$$

Combining the elemental flux equations permits the ratio of any individual flux to the total flux to be written in terms of a function (F_i) of the coupling parameters (see previous examples)

$$\frac{j_i}{J} = F_i(\beta', \theta, \partial) \qquad (A2.4.3)$$

There is mass conservation of both hydrogen and chlorine species in this system in that there is zero net flux of each. For example, for hydrogen

$$j(HCl) + 2j(H_2S) + 2j(H_2) = 0$$

For HCl in equation (A2.2.1)

$$\frac{p_i^b}{P} = \epsilon$$

where ϵ is the pressure fraction of the transporting gas (HCl) in the carrier gas (Ar) plus HCl mixture - see section (3.4.1). For all other species the ratio p_i^b/P is zero as the carrier gas flushes these species away from the open end of the channel. The exponential term in equation (A2.2.1) is expanded and truncated at 0(2) - the error in this approximation is $\leqslant$ 5% when the transport function, $\xi_i < 0.1$. Hence

$$\frac{p_i}{P} = \frac{j_i}{J} \xi_i \qquad (A2.4.4)$$

and

$$\frac{p(HCl)}{P} = \epsilon + \frac{j(HCl)}{J} \xi_{HCl} \qquad (A2.4.5)$$

assuming $\epsilon \xi_{HCl} << 1$.

The transport functions (ξ_i) are written in terms of the experimental parameter, $\hat{\omega}(ZnS)$, and takes the form

$$\xi_i = \frac{\mathring{\omega} RT\ell}{D_i AMP} G(\beta', \theta, \partial) \qquad \text{(A2.4.6)}$$

where G is an universal function of the coupling parameters, M is the molecular mass of ZnS and A is the cross-sectional area of the channel. Combining equations (A2.4.4) to (A2.4.6) the partial pressures are formed

$$p_i = \frac{\mathring{\omega} RT\ell}{D_i AM} F_i G \qquad (i \neq HCl) \qquad \text{(A2.4.7)}$$

$$p_{HCl} = P_\epsilon - \frac{\mathring{\omega} RT\ell}{D_{HCl} AM} F_{HCl} G \qquad \text{(A2.4.8)}$$

Next, the equilibrium constants K_3, K_5 and K_8 are written in terms of the partial pressures and are then equated to the analytical expressions taken from the literature (see Results and Discussion Section (5.5)). The resultant expressions are maniputated so as to solve for the three unknown coupling parameters (θ, ∂ and β') when they are then evaluated at each experimental temperature. These values are then back-substituted in the equation for K_7.

Details of effects of multicomponent diffusion and second order treatment are discussed in Section (3.4.2) and applied in program ZNSHCl10.FOR.

A2.5 Evaporation of Diamminedichlorozinc(II) in Ar

Relevant Computer Program ZNCl22NH3A.FOR

A possible reaction below the melting point of zinc chloride may be written as

$$ZnCl_2 2NH_3(c) \quad = \quad ZnCl_2NH_3(l) + NH_3(g) \qquad\qquad K_5$$

the liberation of one mole of ammonia. The MEM algebraic flux expressions are

sum of all the flux $\sum_i j_i = j(NH_3) = J$

and the emergent flux $j_e = j(NH_3) = \dfrac{\mathring{\omega}_{NH_3}}{AM_{NH_3}}$

but $$\frac{p_{NH_3}}{P} = \frac{j(NH_3)}{J}(1 - e^{-\xi_{NH_3}})$$

where $$\xi_{NH_3} = \frac{\mathring{\omega}RT\ell}{D_{NH_3}AM_{NH_3}P}$$

The partial pressure of ammonia

$$p_{NH_3} = P(1 - e^{-\xi_{NH_3}})$$

and hence K_5 may be determined $K_5 = \left[\dfrac{p_{NH_3}}{p^{\theta}}\right]$

The diffusivity was estimated over the experimental temperature range (438 to 503 K) from the Lennard-Jones potential parameters for Ar and NH_3

$$D(NH_3,Ar)/m^2s^{-1} = 1.825 \times 10^{-5}(T/273.15)^{1.842}$$

Appendix 3

Computer Programs

Mainframe used RHBNC Vax-Cluster 11/780 VMS

Programming language: Fortran 4 and 77

	Program	Comment	Page No.
A3.1	F36SPLOT.FOR	Typical Graphics Routine	233
A3.2	ZINCW.FOR	Zinc in Inert Gases	234
A3.3	MERCURYW.FOR	Mercury in Inert Gases	234
A3.4	ZNCL2HT.FOR	Zinc Chloride Monomer	235
A3.5	ZNCL2K2.FOR	Calculates Dimer	237
A3.6	ZNCL2PG.FOR	MEM data & lit. v. press.	240
A3.7	ZNSDS3G.FOR	Reduction of ZnS in H_2	244
A3.8	ZNSHCL10.FOR	ZnS transport in HCl	247
A3.9	ZNCL22NH3A.FOR	Evaporation of diammine	252
	ZNCL22NH3A.MTB	Simple MINITAB Routine	252

* The zinc chloride simplex routine written by Andrew Wroot (RHBNC) as a general purpose user-friendly program is not included.

```
      program f36splot
C
C...  Programmer P.Pang
C***  Figure 3.6  Binary Gaseous Diffusion Coefficients of
C***              Mercury In Inert Gases      400-600K
C
C...  Plot series of points x(i),y(i) onto simpleplot
C     and their respective regression lines
      dimension x1(100),x2(100),x3(100),x4(100)
      dimension y1(100),y2(100),y3(100),y4(100)
      dimension average1(100),average2(100)
      dimension average3(100),average4(100)
      real a,b
C
C...  Data for Mercury H2(In(T/273.15)),InDt),HE...
      open(unit=7, file='HGH2MTB.OUT',status='old')
      open(unit=8, file='HGHEMTB.OUT',status='old')
      open(unit=9, file='HGN2MTB.OUT',status='old')
      open(unit=10,file='HGARMTB.OUT',status='old')
C
C...  Grouping Data Points For Average Plot
      data (average1(I),I=1,8)/4,10,6,8,7,7,10,10/
      data (average2(I),I=1,7)/4,10,7,9,9,7,7/
      data (average3(I),I=1,8)/6,8,5,6,10,7,6,5/
      data (average4(I),I=1,8)/2,4,3,10,7,8,5,11/
      do j = 1,8
              do i  = 1,average1(j)
              read(7,*)b,a
              x1(j) = x1(j) + a
              y1(j) = y1(j) + b
              end do
      x1(j) = x1(j)/average1(j)
      y1(j) = y1(j)/average1(j)
      end do
      do j = 1,7
              do i  = 1,average2(j)
              read(8,*)b,a
              x2(j) = x2(j) + a
              y2(j) = y2(j) + b
              end do
      x2(j) = x2(j)/average2(j)
      y2(j) = y2(j)/average2(j)
      end do
      do j = 1,8
              do i  = 1,average3(j)
              read(9,*)b,a
              x3(j) = x3(j) + a
              y3(j) = y3(j) + b
              end do
      x3(j) = x3(j)/average3(j)
      y3(j) = y3(j)/average3(j)
      end do
      do j = 1,8
              do  i = 1,average4(j)
              read(10,*)b,a
              x4(j) = x4(j) + a
              y4(j) = y4(j) + b
              end do
```

```
      x4(j) = x4(j)/average4(j)
      y4(j) = y4(j)/average4(j)
      end do
C
C...  Size of Picture in (x,y)
      call picsiz(12.0,19.0)
C
C  ***Set character format = 1 OR graph landscape by default***
      call    chset(1)
C
C...  Choose line eg regression (4) or quadratic (5)
      ntype = 4
C
C...  Scale (xi,xz,1,yi,yz,1)
      call    scales(0.42,0.80,1,-10.85,-8.50,1)
      call    xscale(0.42,0.80,1)
      call    yscale(-10.85,-8.50,1)
C
C...  Set page in cm eg A4(21.0,29.7)   A4(x,y)
      call    page(21.0,29.7)
C
C...  Define axes(x,y)
      call    axes7('In (D/m  s ) ','In (T/273.15) ')
C     call axes7('x','Y')
      call    cv type(ntype)
      do i = 1,8
      call mark pt(x1(i),y1(i),0)
      end do
      do i = 1,7
      call mark pt(x2(i),y2(i),1)
      end do
      do i = 1,8
      call mark pt(x3(i),y3(i),2)
      end do
      do i = 1,8
      call mark pt(x4(i),y4(i),5)
      end do
C
      call brkn cv(x1,y1,8,1)
      call brkn cv(x2,y2,7,2)
      call brkn cv(x3,y3,8,3)
      call brkn cv(x4,y4,8,-1)
C
      CALL SET KY('B','R',4,14)
      call both k7( 1,0,'D(Hg,H2) 62pts')
      call both k7( 2,1,'D(Hg,He) 53pts')
      call both k7( 3,2,'D(Hg,N2) 53pts')
      call both k7(-1,5,'D(Hg,Ar) 50pts')
C...
C...  Title
      call    title7('l','c',' Figure 3.6  Binary Gaseous
     * Diffusion Coefficients of')
      call    title7('l','c',' .             Mercury in Ine
     *rt Gases  420-600 K      .')
C
      call    endplt
      stop
      end
```

```
      PROGRAM ZINCW
C...  PROGRAMMER P.PANG
C...  BINARY GASEOUS DIFFUSION COEFFICIENTS OF ZINC IN
C...  HYDROGEN,HELIUM,ARGON,AND NITROGEN.
C...   TEMPERATURE RANGE 720-1120K.
C
C...  PROGRAM CALCULATES DIFFUSION COEFFICIENTS OF ZINC IN INERT
C...  GAS AS A FUNCN OF TEMP. DATA STORED ON ZINCW.OUT (Dt,T,XXI)
C...  INDIVIDUAL FILES NEEDS TO BE MADE UP FROM ZNH2.EMF,ZNN2.EMF ETC.,
C...  INTO ZNH2AA.EMF,ZNH2BB.EMF...,ZNN2AA.EMF,ZNN2BB.EMF...,ETC.
      REAL L2,R2,BETA,PI,R,PO,MZN
      REAL RN(100),EMF(100),TC(100),MLNW(100),P(100),WDOTE(100)
      REAL LNPZN(100),PZN(100),XXX,YYY,DT,XXI
      INTEGER I,II
      CHARACTER*80 HEADER(100),FILENM
      TYPE 100
 100  FORMAT('  ENTER ZINC/INERT GAS DATA FILE.e.g. ZNH2AA.EMF :'$)
      READ(5,'(A80)')FILENM
      OPEN(UNIT=8,FILE=FILENM,STATUS='OLD')
      OPEN(UNIT=7,FILE='ZINCW.OUT',STATUS='NEW')
              DO I =1,10
              READ(8,'(A80)')HEADER(I)
              WRITE(6,'(1X,A80)')HEADER(I)
              END DO
      WRITE(6,*)'ENTER L2,R2,BETA CORR IN METERS'
      READ(5,*) L2,R2,BETA
      PI=4.00*ATAN(1.000)
      R =8.314200
      PO=101325.00
      MZN=65.3700E-3
C
      DO II=1,100
      READ(8,*)RN(II),EMF(II),TC(II),MLNW(II),P(II)
      IF(RN(II).EQ.0)GOTO 999
      WDOTE(II)=EXP(-MLNW(II))
          P(II)=P(II)*PO/760.00
      IF(TC(II).LT.488.0)THEN
         TC(II)=-0.759-0.00643*TC(II)+TC(II)+273.15
         ELSE IF(TC(II).LT.587.0)THEN
         TC(II)=-3.6+TC(II)+273.15
         ELSE
         TC(II)=-10.9+0.012*TC(II)+TC(II)+ 273.15
      END IF
      LNPZN(II)=-5.7941 -(5330.735/TC(II))- 1.61644E-3*TC(II)
    + +5.59972*ALOG10(TC(II))
      PZN(II)  =(10.0**LNPZN(II))
          XXX  =-WDOTE(II)*R*TC(II)*L2*BETA
          YYY  =P(II)*MZN*PI*(R2**2)*ALOG(1-(PZN(II)/P(II)))
           DT  =XXX/YYY
           XXI  =WDOTE(II)*R*TC(II)*L2/(DT*P(II)*MZN*PI*(R2**2))
      WRITE(7,*)DT,TC(II),XXI
      END DO
 999  WRITE(6,*)' '
      WRITE(6,*)' DATA STORED ON FILE ZINCW.OUT : D,TK,XXI'
      WRITE(6,*)' MINITAB EXEC ZINCW.MTB'
      STOP
      END
```

```
      PROGRAM MERCURYW
C...
C...  PROGRAMMER  P.PANG.
C...  BINARY GASEOUS DIFFUSION COEFFICIENTS OF MERCURY IN
C...  HYDROGEN,ARGON,AND NITROGEN. TEMPERATURE RANGE 423-593K.
C
C...  PROGRAM CALCULATES DIFFUSION COEFFICIENTS OF MERCURY IN INERT
C...   GAS AS A FUNCTION OF TEMPERATURE. DATA IS STORED ON MERCURY.OUT
C...   (Dt,Tk,xxi)
C
      REAL L2,R2,PI,R,PO,MHG
      REAL RN(100),EMF(100),TK(100),MLNW(100),P(100),WDOTE(100)
      REAL LNPHG(100),PHG(100),XXX,YYY,DT,XXI
      INTEGER I,II
      CHARACTER*80 HEADER(100),FILENM
 100  FORMAT('  ENTER MERCURY/INERT GAS DATA FILE.e.g. HGH2B.EMF :'$)
 110  FORMAT('  ENTER CHANNEL DIMENSIONS IN SI UNITS  L2  R2 :'$)
      TYPE 100
      READ(5,'(A80)')FILENM
      OPEN(UNIT=8,FILE=FILENM,STATUS='OLD')
      OPEN(UNIT=7,FILE='MERCURYW.OUT',STATUS='NEW')
C
              DO I =1,10
              READ(8,'(A80)')HEADER(I)
              WRITE(6,'(1X,A80)')HEADER(I)
              END DO
      TYPE 110
      READ(5,*)L2,R2
      PI = 4.00*ATAN(1.000)
      R  = 8.314200
      PO = 101325.00
      MHG= 200.59E-3
      WRITE(6,*)' DT       TK       XXI'
C
      DO II=1,100
      READ(8,*)RN(II),EMF(II),TK(II),MLNW(II),P(II)
      IF(RN(II).EQ.0)GOTO 999
      WDOTE(II) = EXP(-MLNW(II))
      P(II)     = P(II)*PO/760.0
C MERCURY VAPOUR PRESSURE REF.  D.AMBROSE & C.H.S.SPRAKE,
C J. Chem. Thermodynamics 1972, 4, 603-620
C Temperature range 400-686K in kPa needs to be changed to Pa
      LNPHG(II) = 7.658791 - 3279.230/TK(II) -9.680031E-4*TK(II)
    + +4.115463E-7*(TK(II)**2.0E0)
      PHG(II)   = (10.0**LNPHG(II))*1000.0E0
      XXX       = -WDOTE(II)*R*TK(II)*L2
      YYY       = P(II)*MHG*PI*(R2**2)*ALOG(1-(PHG(II)/P(II)))
      DT        = XXX/YYY
       XXI       = WDOTE(II)*R*TK(II)*L2/(DT*P(II)*MHG*PI*(R2**2))
      WRITE(7,*)DT,TK(II),XXI
      WRITE(6,*)DT,TK(II),XXI
      END DO
C
 999  WRITE(6,*)' '
      WRITE(6,*)' DATA STORED ON FILE MERCURYW.OUT : D,TK,XXI'
      WRITE(6,*)' MINITAB  EXECUTE MERCURYW.MTB  '
      STOP
      END
```

```
      PROGRAM ZNCL2HT
C  MAIN PROGRAMMER  P.J.GARDNER   JUNIOR  PROGRAMMER P.PANG
C
C  PROGRAM TO EXTRACT PO(ZNCL2) FROM HIGH/LOW TEMP. ZNCL2
C  TRANSPORT RESULTS USING
C         1) THE EXACT EQN.(NO EXP. APPROXIMATION)
C         2) POINTS OVER 900 K ONLY (FOR KC) OR OTHERWISE
C         3) NO GAMMA CORRECTIONS AS 2-COMPONENT SYSTEM ASSUMED
C
C  SELECT RELEVANT DATA FROM
C  ZNCL2AR.EMF etc.
C
      REAL M(20)
      REAL L2,K1(200),MLNW
      INTEGER C,C1,RN(200),M2(10)
      CHARACTER*80  J1,HEADER(100)
      DIMENSION P(200),TC(200),TK(200),DA1(200)
      DIMENSION G1(200),WDOTE(200),MLNW(200)
      REAL LOWEST,HIGHEST
      COMMON TK,K1,R
      PI=4.*ATAN(1.0)
      PRINT*,'How many data sets?  Assign as FOR001,FOR002....'
      READ*,M1
      PRINT*,'Enter 10^6Do and 1+s'
      READ*,DOA,OPS
      PRINT*,'ENTER TEMP RANGE LOWEST  HIGHEST IN K'
      READ*,LOWEST,HIGHEST
      MO=0
      C1=0
      DO 887 J=1,M1
      MO=MO+1
      PRINT*,'Enter r , l, and # of data points  for data set ',J
      READ*,R2,L2,M2(J)
      READ(MO,888)(HEADER(I),I=1,10)
 888  FORMAT(A80)
      DO I=1,M2(J)
      C1       =       C1+1
      READ(MO,*)RN(C1),EMF,TC(C1),MLNW(C1),P(C1)
C   TEMP CORRECTION FOLLOWS
      TC(C1)    =      TC(C1)-2.4-0.002*TC(C1)
      TK(C1)    =      TC(C1)+273.15
      WDOTE(C1)=EXP(-MLNW(C1))
C   SCALE TO UNIT CHANNEL
      WDOTE(C1)          =        WDOTE(C1)*L2/(PI*R2*R2)
      P(C1)     =      P(C1)*101325./760.
      ENDDO
 887  CONTINUE
C TEST PRINT
      PRINT*,'Some typical data points'
      print*,'______________________'
      DO I=1,C1,10
      PRINT*,I,RN(I),TK(I),P(I)
      ENDDO
      PRINT*,'____________________________________'
      PRINT*,C1,' data points combined'
      PRINT*,'____________________________________'
      DATA BETA,M(1)/1.0,0.13628/
C  SORT OUT HT RESULTS
      C      = 0
      DO 886 I=1,C1
      IF(TK(I).LT.LOWEST .OR. TK(I).GT.HIGHEST)GOTO 886
C     IF(TK(I).LT.900.0)GOTO 886
      C               =         C+1
      RN(C)     =        RN(I)
      TK(C)     =        TK(I)
      P(C)      =        P(I)
      WDOTE(C) =         WDOTE(I)
 886  CONTINUE
      N               =         C
      PRINT*,'  '
      PRINT*,N,' data points selected'
      print*,'____________________________________'
C  STORE G1 AS OPTION TO USE LATER
      DATA(G1(I),I=1,28)/6*0.946,7*0.927,8*0.899,7*0.860/
      R               =         8.3143
      PO        =        101325.
      WRITE(6,992)
 992  FORMAT(X,'HIGH TEMP. (T>900 K) ZNCL2/AR DATA ')
      WRITE(6,991)
 991  FORMAT(' ***************************************************')
      WRITE(6,998)
 998  FORMAT(X,' T/K     WDOTE          E1           K1')
 100  CONTINUE
      DO 50 I=1,N
      TO        =        TK(I)/273.15
      DOA1      =        DOA*1.E-6*TO**OPS
      DA1(I)    =        DOA1
      R2        =        1.
      L2        =        1.
      W               =         R2*R2*M(1)/(R*TK(I)*L2*BETA)
      E1        =        WDOTE(I)/(W*DA1(I)*P(I))
      K1(I)     =        P(I)*(1.-EXP(-E1))/PO
      WRITE(6,999)TK(I),WDOTE(I),E1,K1(I)
 999  FORMAT(X,F6.2,XX,E10.5,XX,F7.4,XX,F10.4)
50    CONTINUE
      CALL LS(N,AO,BO,EO,DO,R3,R5)
      WRITE(6,890)
 890  FORMAT(//,X,'IN FOLLOWING LS ANALYSIS,Y = DELTA(G) AND X =T/K')
      WRITE(6,889)
 889  FORMAT(X,'*****************************************************')
```

```
      WRITE(6,891)
 891  FORMAT(' LEAST SQUARES ANALYSIS: Y=BOX+AO '/
     +' ------------------------------------',//)
      WRITE(6,896)AO
 896  FORMAT(' AO= ',F15.5)
      WRITE(6,895)BO
 895  FORMAT(' BO= ',F15.5)
      WRITE(6,894)EO
 894  FORMAT(' S.D.(AO)= ',F15.5)
      WRITE(6,893)DO
 893  FORMAT(' S.D.(BO)= ',F15.5)
      WRITE(6,892)R5
 892  FORMAT(' CORRELATION COEFFT.= ',F8.6///)
        STOP
        END
      SUBROUTINE LS(N,AO,BO,EO,DO,R3,R5)
C *** LEAST SQUARES ON STRAIGHT LINE IN FORM Y=BOX+AO.
C *** GIVES GRADIENT(BO), INTERCEPT(AO), THEIR
C *** STANDARD DEVIATIONS AND A CORRELATION COEFFICIENT
      DIMENSION X1(200),Y1(200)
      REAL K1(200)
      COMMON TK(200),K1,R
        DO 10 I=1,N
        X1(I)=TK(I)
        Y1(I)=-R*X1(I)*ALOG(K1(I))
 10     CONTINUE
      S1=0.
      S2=0.
      S3=0.
      S4=0.
      S5=0.
      S6=0.
      S7=0.
      DO 30 I=1,N
      SO=X1(I)
      S1=S1+SO
      S2=Y1(I)
      S3=S3+S2
      S4=X1(I)*Y1(I)
      S5=S5+S4
      S6=X1(I)*X1(I)
      S7=S7+S6
 30   CONTINUE
      FN=FLOAT(N)
      CO=S1*S1-FN*S7
      BO=(S3*S1-FN*S5)/CO
      AO=(S5*S1-S3*S7)/CO
      XO=S1/FN
      YO=S3/FN
      S8=0.
      S9=0.
      TO=0.
      T1=0.
      T2=0.
      T3=0.
      T4=0.
      T5=0.
      DO 40 I=1,N
      S8=(X1(I)-XO)**2
      S9=S9+S8
      TO=(Y1(I)-BO*X1(I)-AO)**2
      T1=T1+TO
      T2=(Y1(I)-YO)**2
      T3=T3+T2
      T4=(X1(I)-XO)*(Y1(I)-YO)
      T5=T5+T4
 40   CONTINUE
      DO=SQRT(T1/((FN-2.)*S9))
      EO=SQRT(T1*S7/(FN*(FN-2.)*S9))
      R4=(BO**2)*S9/T3
      R3=SQRT(R4)
      R5=T5/SQRT(S9*T3)
      RETURN
      END
```

```
      PROGRAM ZNCL2K2
C  MAIN PROGRAMMER  P.J.GARDNER    JUNIOR PROGRAMMER P.PANG
C
C  PROGRAM TO EXTRACT K2(T)) FROM LOW TEMP. ZNCL2
C  TRANSPORT RESULTS USING
C          1)  H1 & S1 FROM ZNCL2HT.FOR/ZNCL2AR.EMF (OR ELSEWHERE)
C              ARE SET INTERACTIVELY
C          2)  POINTS BELOW 900 K ONLY OR OTHERWISE
C          3)  FULL GAMMA CORRECTIONS
C          4)  IN EXP. EXPN., TRUNCATE AT O(3) NOT O(2)
C  SELECT RELEVANT DATA FROM ZNCL2AR.EMF
      REAL M(20)
      REAL L2,K1(200),MLNW,K2(200)
      INTEGER C,C1,RN(200),M2(10)
      CHARACTER*80  J1,HEADER(100)
      DIMENSION P(200),TC(200),TK(200),DA1(200),P1(200),P2(200)
      DIMENSION DA2(200),WDOTE(200),MLNW(200)
      COMMON/LS/ TK,K2,R
      COMMON/GAMMA/E1,E2,ALPHA(200),D(20,20)
      PI=4.*ATAN(1.0)
      PRINT*,'How many data sets?  Assign as FOR001,FOR002....'
      READ*,M1
      PRINT*,'Enter 10^6D12, 10^6D24, 1+s1, & 1+s2'
      READ*,D12,D24,OPS1,OPS2
      PRINT*,'Enter H1/J mol-1 and S1/J mol-1K-1'
      READ*,H1,S1
C Convert H1 and S1 to appropriate temperature
      PRINT*,'Enter the ZNCL2K2 points ref. temperature'
      print*,'followed by the ZNCL2HT ref. temperature'
      READ*,TEMP2,TEMP1
      H1=H1-40.55*(TEMP2-TEMP1)+0.42E-3*(TEMP2**2-TEMP1**2)
      S1=S1-40.55*ALOG(TEMP2/TEMP1)+.00084*(TEMP2-TEMP1)
      MO=0
      C1=0
      DO 887 J=1,M1
      MO=MO+1
      PRINT*,'Enter r , l, and # of data points  for data set ',J
      READ*,R2,L2,M2(J)
      READ(MO,888)(HEADER(I),I=1,10)
 888  FORMAT(A80)
      DO I=1,M2(J)
      C1=C1+1
      READ(MO,*)RN(C1),EMF,TC(C1),MLNW(C1),P(C1)
C     TEMP CORRECTION FOLLOWS
      TC(C1)=TC(C1)-2.4-0.002*TC(C1)
      TK(C1)=TC(C1)+273.15
      WDOTE(C1)=EXP(-MLNW(C1))
C     SCALE TO UNIT CHANNEL
      WDOTE(C1)=WDOTE(C1)*L2/(PI*R2*R2)
      P(C1)=P(C1)*101325./760.
```

```
      ENDDO
 887  CONTINUE
      PRINT*,C1,' data points read in'
      PRINT*,'*******************************************'
      PRINT*,'Some typical points:-'
      DO I=1,C1,10
      PRINT*,I,RN(I),TC(I),TK(I),P(I)
      ENDDO
      DATA BETA/1.0/
      DATA(M(I),I=1,11)/0.136276,0.272552,100.,100.,100.,100.,
     +100.,100.,100.,100.,0.039948/
C  SORT OUT LT RESULTS
      C=0
      DO 886 I=1,C1
      IF(TK(I).GE.900.0)GOTO 886
      C=C+1
      TK(C)=TK(I)
      P(C)=P(I)
      WDOTE(C)=WDOTE(I)
      RN(C)=RN(I)
 886  CONTINUE
      N=C
      NO=C
      PRINT*,NO,' data points selected'
      DO 120 I=1,11
      DO 130 J=1,11
      D(I,J)=SQRT(M(J)/M(I))-1.
 130  CONTINUE
 120  CONTINUE
      R=8.3143
      PO=101325.
      WRITE(6,992)
 992  FORMAT(X,'LOW TEMP. (T<900 K) ZNCL2/AR DATA ')
      WRITE(6,991)
 991  FORMAT(' ****************************************************')
      WRITE(6,882)H1,S1
 882  FORMAT(X,'USING H1= ',F8.1,'Jmol-1 and S1= ',F6.1,'JK-1mol-1')
      WRITE(6,991)
      WRITE(6,998)
 998  FORMAT(X,'   T/K     ALPHA       K2(T)    GA1    GA2',
     +'    E1     E2       %     K')
      DO 50 I=1,N
      TO=TK(I)/273.15
      K1(I)=EXP(S1/R-H1/(R*TK(I)))
C
C  FORM INITIAL DIFF. COEFFTS.(DOA1 & DOA2), AND FIRST GUESSES FOR
C  GAMMA, CALLED T1 & T2
      DOA1     =       D12*1.E-6*TO**OPS1
      DOA2     =       D24*1.E-6*TO**OPS2
      DA1(I)   =       DOA1
```

```
      DA2(I)    =      DOA2
      T1        =      1.0
      T2        =      1.0
      L2        =      1.
      R2        =      1.
      W         =            R2*R2*M(1)/(R*TK(I)*L2*BETA)
      K         =            0
 110  K         =            K+1
C  FORM FIRST GUESSES FOR E1 AND E2 AND ALPHA
      E1BAR     =      WDOTE(I)/(W*DA1(I)*P(I))
      E2BAR     =      WDOTE(I)/(W*DA2(I)*P(I))
C  ALPHA IS NOW FORMED FROM THE ROOT OF A QUADRATIC BECAUSE OF
C  THE O(3) TRUNCATION
      A0        =      K1(I)*P0/P(I)
      B0        =      E1BAR
      A2        =      2.*A0-2.*B0+B0*B0
      B2        =      8.*A0-4.*B0+B0*B0
      C2        =      8*A0
      A3        =      B2*B2-4.*A2*C2
      IF(A3.LT.0.0)THEN
         ALPHA(I)=99.
      ELSE
         ALPHA(I)=(-B2-SQRT(A3))/(2.*A2)
      ENDIF
      F                =     (ALPHA(I)+1.)/(ALPHA(I)+2.)
      E1        =      E1BAR*F
      E2        =      E2BAR*F
      CALL GAMMA(GA1,GA2,I)
      IF (ABS((GA1-T1)/T1).LE.0.0001.AND.ABS((GA2-T2)/T2).LE.
     +0.0001)THEN
  49  DA1(I)    =      DOA1/GA1
      DA2(I)    =      DOA2/GA2
      B0        =      WDOTE(I)/(W*DA1(I)*P(I))
      A2        =      2.*A0-2.*B0+B0*B0
      B2        =      8.*A0-4.*B0+B0*B0
      C2        =      8.*A0
      A3        =      B2*B2-4.*A2*C2
      IF(A3.LT.0.0)THEN
          ALPHA(I)=99.
      ELSE
          ALPHA(I)=(-B2-SQRT(A3))/(2.*A2)
      ENDIF
      F                =     (ALPHA(I)+1.)/(ALPHA(I)+2.)
      E1        =      WDOTE(I)*F/(W*DA1(I)*P(I))
      E2        =      E1*DA1(I)/DA2(I)
      P1(I)     =ALPHA(I)*P(I)*(1.-EXP(-E1))/(ALPHA(I)+1.)
      P2(I)     =      P(I)*(1.-EXP(-E2))/(ALPHA(I)+1.)
      K2(I)     =      P2(I)*P0/(P1(I)*P1(I))
C  FORM ALPHAO, THE % DIMER IN GAS
      ALPHAO    =      100*P2(I)/(P2(I)+P1(I))
```

```
      WRITE(6,885)TK(I),ALPHA(I),K2(I),GA1,GA2,E1,E2,ALPHAO,K
 885  FORMAT(X,F7.2,X,E10.3,X,E10.4,X,4(F6.3,X),F8.3,I3)
      ELSE
              T1=GA1
              T2=GA2
C  PROTECTION AGAINST SPURIOUS VALUES- RESTART REITERATION
              IF(T1.LE.0.0)T1=0.9
              IF(T2.LE.0.0)T2=0.9
              DA1(I)=DOA1/T1
              DA2(I)=DOA2/T2
C  PROTECTION AGAINST CONTINUOUS LOOPING
               IF(K.GE.100)GOTO 49
              GO TO 110
      ENDIF
  50  CONTINUE
C PRINT OUT PARTIAL PRESSURES
      WRITE(6,878)
 878  FORMAT(X,'   T/K        P1           P2',
     +'       K1           K2')
      WRITE(6,991)
      DO I=1,N
      WRITE(6,879)TK(I),P1(I),P2(I),K1(I),K2(I)
 879  FORMAT(X,F7.2,XX,F9.1,XX,F9.1,XX,E10.4,XX,E10.4)
      ENDDO
      WRITE(6,884)
 884  FORMAT(X,'THE FOLLOWING DATA POINTS WERE REJECTED:-',//,
     +'   I   T/K       WDOTE      K2')
      L=0
      DO I=1,N
      IF(K2(I).LE.0.)THEN
        WRITE(6,883)I,TK(I),WDOTE(I),K2(I)
 883    FORMAT(X,I3,X,F7.2,XX,E9.3,XX,E9.3)
      ELSE
        L=L+1
        TK(L)=TK(I)
        K2(L)=K2(I)
      ENDIF
      ENDDO
      N=L
      WRITE(6,881)N,NO
 881  FORMAT(X,/,' NUMBER OF USED POINTS= '.I3,' FROM ',I3,//)
      CALL LS(N,A0,B0,E0,D0,R5)
        PRINT*,'    '
        WRITE(6,880)D12,D24,OPS1,OPS2
 880    FORMAT(X,'  D12=  ',F6.3,'  D24= ',F6.3,' 1+s1= ',
     +F5.3,'  1+s2=  ',F5.3)
        PRINT*,'_______________________________________________'
        WRITE(6,877)TEMP2,H1,TEMP2,S1
 877    FORMAT(X,' H1(',F4.0,')=',F8.0,'    S1(',F4.0,')=',F6.1)
        PRINT*,'*********************************************'
```

```
       WRITE(6,890)
890    FORMAT(/,X,'IN FOLLOWING LS ANALYSIS,Y = DELTA(G) AND X =T/K')
       WRITE(6,889)
889    FORMAT(X,'****************************************************')
       WRITE(6,891)
891  FORMAT(' LEAST SQUARES ANALYSIS: Y=BOX+AO '/
    +' ---------------------------------',/)
     WRITE(6,896)AO
896  FORMAT(' AO= ',F15.5)
     WRITE(6,895)BO
895  FORMAT(' BO= ',F15.5)
     WRITE(6,894)EO
894  FORMAT(' S.D.(AO)= ',F15.5)
     WRITE(6,893)DO
893  FORMAT(' S.D.(BO)= ',F15.5)
     WRITE(6,892)R5
892  FORMAT(' CORRELATION COEFFT.= ',F8.6///)
       STOP
       END
     SUBROUTINE LS(N,AO,BO,EO,DO,R5)
C *** LEAST SQUARES ON STRAIGHT LINE IN FORM Y=BOX+AO.
C *** GIVES GRADIENT(BO), INTERCEPT(AO), THEIR
C *** STANDARD DEVIATIONS AND A CORRELATION COEFFICIENT
     DIMENSION X1(200),Y1(200)
     REAL K2(200)
     COMMON/LS/ TK(200),K2,R
       DO 10 I=1,N
       X1(I)=TK(I)
       Y1(I)=-R*X1(I)*ALOG(K2(I))
10     CONTINUE
     S1=0.
     S2=0.
     S3=0.
     S4=0.
     S5=0.
     S6=0.
     S7=0.
     DO 30 I=1,N
     SO=X1(I)
     S1=S1+SO
     S2=Y1(I)
     S3=S3+S2
     S4=X1(I)*Y1(I)
     S5=S5+S4
     S6=X1(I)*X1(I)
     S7=S7+S6
30   CONTINUE
     FN=FLOAT(N)
     CO=S1*S1-FN*S7
     BO=(S3*S1-FN*S5)/CO
```

```
      AO=(S5*S1-S3*S7)/CO
      XO=S1/FN
      YO=S3/FN
      S8=0.
      S9=0.
      TO=0.
      T1=0.
      T2=0.
      T3=0.
      T4=0.
      T5=0.
      DO 40 I=1,N
      S8=(X1(I)-XO)**2
      S9=S9+S8
      TO=(Y1(I)-BO*X1(I)-AO)**2
      T1=T1+TO
      T2=(Y1(I)-YO)**2
      T3=T3+T2
      T4=(X1(I)-XO)*(Y1(I)-YO)
      T5=T5+T4
  40  CONTINUE
      DO=SQRT(T1/((FN-2.)*S9))
      EO=SQRT(T1*S7/(FN*(FN-2.)*S9))
      R4=(BO**2)*S9/T3
      R3=SQRT(R4)
      R5=T5/SQRT(S9*T3)
      RETURN
      END
      SUBROUTINE GAMMA(GA1,GA2,I)
      REAL J1J,J2J
      COMMON/GAMMA/ E1,E2,ALPHA(200),D(20,20)
      J1J=ALPHA(I)/(1.+ALPHA(I))
      J2J=1./(1.+ALPHA(I))
      B1=0.5*(D(11,2)*D(1,2)*J2J-1.)
      B2=0.5*(D(11,1)*D(2,1)*J1J-1.)
      GA1=1.+B1*E1
      GA2=1.+B2*E2
      RETURN
      END
```

```
      PROGRAM ZNCL2PG
C
C
C***   MAIN    PROGRAMMER P.J. GARDNER
C      JUNIOR  PROGRAMMER P.PANG
C
C PROGRAM TO SELECT RHBNC RESULTS IN K&Cs TEMP RANGE.
C THEN COMBINES P1+P2 FROM K&C WITH D1P1+2D2P2 FROM
C RHBNC TO EXTRACT P1 AND P2
C KC KENESHEA & CUBICCIOTTI
C
C  SELECT RELEVANT DATA FROM
C  ZNCL2AR.EMF etc
C
C MODIFIED TO PROCESS COMBINED DATA SETS , EACH WITH
C DIFFERENT R AND L, AND REGRESS RESULTS
C
C   WITH GAMMA CORRECTIONS
C
      REAL M(20)
      REAL L2,MLNW,J1J,J2J
      INTEGER C,C1,RN(200),BRIEF,M2(10)
      CHARACTER*80  J1,HEADER(100)
      DIMENSION P(200),TC(200),TK(200),DA1(200),DA2(200)
      DIMENSION WDOTE(200),MLNW(200)
      DIMENSION P1(200),P2(200),PC(200)
      DIMENSION D(11,11)
      REAL RANGE1,RANGE2
      COMMON/LS/TK,PC,R
C
C READ MEM ZNCL2AR.EMF DATA
      PRINT*,'How many data sets?  Assign as FOR001,FOR002....'
      READ*,M1
      PRINT*,'Enter 10^6D12, 10^6D24, 1+s1, and 1+s2'
      READ*,D12,D24,OPS1,OPS2
      PRINT*,'ENTER A AND B IN LOG10(PTmm)=A-B/T '
      READ*,A,B
      PRINT*,'Brief output?   0=NO   1=YES'
      READ*,BRIEF
      PRINT*,'ENTER TEMP RANGE  LOWEST  HIGHEST'
      READ*,RANGE1,RANGE2
C
      PI      =       4.*ATAN(1.0)
      MO      =       0
      C1      =       0
C
      DO 887 J=1,M1
      MO          =        MO+1
      PRINT*,'Enter r , l, and # of data points  for data set ',J
      READ*,R2,L2,M2(J)
      READ(MO,888)(HEADER(I),I=1,10)
 888  FORMAT(A80)
      DO I=1,M2(J)
      C1          =        C1+1
      READ(MO,*)RN(C1),EMF,TC(C1),MLNW(C1),P(C1)
C
C   TEMP CORRECTION FOLLOWS
      TC(C1)    =          TC(C1)-2.4-0.002*TC(C1)
      TK(C1)    =          TC(C1)+273.15
      WDOTE(C1)            =        EXP(-MLNW(C1))
C
C   SCALE TO UNIT CHANNEL
      WDOTE(C1)            =        WDOTE(C1)*L2/(PI*R2*R2)
      P(C1)       =        P(C1)*101325./760.
      ENDDO
 887  CONTINUE
C
C TEST
      IF(BRIEF.EQ.1)GOTO 875
      PRINT*,'Some typical data:'
      PRINT*,'            I            RN       T/K              P'
      DO I=1,C1,10
      PRINT*,I,RN(I),TK(I),P(I)
      ENDDO
 875  CONTINUE
      PRINT*,'______________________________________'
      PRINT*,C1,' data points combined'
      PRINT*,'______________________________________'
      DATA BETA/1.0/
      DATA(M(I),I=1,11)/.13628,.27256,8*100.,.039948/
      DO 120 I=1,11
      DO 130 J=1,11
      D(I,J)=SQRT(M(J)/M(I))-1.
 130  CONTINUE
 120  CONTINUE
C
C  SORT OUT  RESULTS IN COMMON RANGE
      C                  =       0
      DO 886 I=1,C1
      IF((TK(I).LT.RANGE1).OR.(TK(I).GT.RANGE2))GOTO 886
      C                  =       C+1
      TK(C)     =        TK(I)
      P(C)      =        P(I)
      WDOTE(C) =         WDOTE(I)
      RN(C)     =        RN(I)
 886  CONTINUE
      IF(BRIEF.EQ.1)GOTO 880
      PRINT*,'Results in common range'
      PRINT*,'***********************'
 880  CONTINUE
```

```
      N                 =      C
      PRINT*,'    '
      PRINT*,N,' data points selected'
      print*,'_________________________________'
      R                 =      8.3143
      PO        =       101325.
      IF(BRIEF.EQ.1)GOTO 879
      WRITE(6,*)'TEMP RANGE SELECTED FOR ZNCL2/AR DATA IN K'
      WRITE(6,*)RANGE1,RANGE2
      WRITE(6,991)
 991  FORMAT(' *************************************************')
      WRITE(6,882)
 882  FORMAT(X,'   T/K            PT             P1     ',
     +'      P2         P2/PT     GA1      GA2      K')
      WRITE(6,991)
 879  CONTINUE
C
C***
C***  SET UP DIFFUSION COEFFICIENTS
      DO 50 I=1,N
      TO=TK(I)/273.15
      L2        =       1.
      R2        =       1.
      V                 =      R2*R2*M(1)/(R*TK(I)*L2*BETA)
      DOA1      =       1.E-6*D12*TO**OPS1
      DOA2      =       1.E-6*D24*TO**OPS2
      DA1(I)    =       DOA1
      DA2(I)    =       DOA2
      T1        =       1.
      T2        =       1.
      K                 =      0
 100  K                 =      K+1
      X                 =      WDOTE(I)/W
      PT        =       10.**(A-B/TK(I))
      PT        =       PT*PO/760.
      P2(I)     =       (X-DA1(I)*PT)/(2*DA2(I)-DA1(I))
      P1(I)     =       PT-P2(I)
C*** AL(j(Zn2Cl4)/j(ZnCl2)),E1(xi(ZnCl2)),J1J(j1/J)
      AL        =       DA1(I)*P1(I)/(DA2(I)*P2(I))
      ALR       =       (AL+1.)/(AL+2.)
      E1        =       X*ALR/(DA1(I)*P(I))
      E2        =       X*ALR/(DA2(I)*P(I))
      J1J       =       AL/(1.+AL)
      J2J       =       1./(1.+AL)
C*** Gamma correction
      B1        =       0.5*(D(11,2)*D(1,2)*J2J-1.)
      B2        =       0.5*(D(11,1)*D(2,1)*J1J-1.)
      GA1       =       1.+B1*E1
      GA2       =       1.+B2*E2
C
      IF((ABS((GA1-T1)/T1).LE..001).AND.(ABS((GA2-T2)/T2)
     +.LE..001))THEN
 49   DA1(I)    =       DOA1/GA1
      DA2(I)    =       DOA2/GA2
      P2(I)     =       (X-DA1(I)*PT)/(2*DA2(I)-DA1(I))
      P1(I)     =       PT-P2(I)
      IF(BRIEF.EQ.1)GOTO 878
      WRITE(6,884)TK(I),PT,P1(I),P2(I),P2(I)/PT,GA1,GA2,K
 884  FORMAT(X,F7.3,XXX,F9.1,XXX,F9.1,XXX,F9.1,XXX,F9.4,XXX,2(F6.3,
     +XX),I3)
 878  CONTINUE
      ELSE
      T1        =       GA1
      T2        =       GA2
      DA1(I)    =       DOA1/T1
      DA2(I)    =       DOA2/T2
      IF(K.EQ.25)GOTO 49
      GOTO 100
      ENDIF
 50   CONTINUE
      IF(BRIEF.EQ.1)GOTO 877
      PRINT*,'THE FOLLOWING DATA WERE REJECTED'
      PRINT*,'          I       T/K             P1              P2'
 877  CONTINUE
      L                 =      0
C
      DO I=1,N
      IF((P2(I).LE.0).OR.(P1(I).LE.0))THEN
      IF(BRIEF.EQ.1)GOTO 876
      PRINT*,I,TK(I),P1(I),P2(I)
 876  CONTINUE
      ELSE
      L=L+1
      TK(L)=TK(I)
      P2(L)=P2(I)
      P1(L)=P1(I)
      ENDIF
      ENDDO
      WRITE(6,885)N-L,N
 885  FORMAT(X,/,' Number of points rejected is ',I3,' from '
     +,I3,//)
      IF(L.LT.3)THEN
      PRINT*,'TOO FEW POSTIVE POINTS!'
      STOP
      ENDIF
      N=L
      IF(BRIEF.EQ.1)GOTO 874
      PRINT*,'LS FOR P1'
      PRINT*,'*********'
      PRINT*,'      '
```

```
 874  CONTINUE
      DO I=1,N
      PC(I)=P1(I)/P0
      ENDDO
C
      CALL LS(N,A0,B0,E0,D0,R5)
      L1=0
 883  L1=L1+1
      IF(BRIEF.EQ.1)GOTO 873
      WRITE(6,890)
 890  FORMAT(//,X,'IN FOLLOWING LS ANALYSIS,Y = DELTA(G) AND X =T/K')
      WRITE(6,889)
 889  FORMAT(X,'**************************************************')
      WRITE(6,891)
 891  FORMAT(' LEAST SQUARES ANALYSIS: Y=BOX+A0 '/
     +' ---------------------------------',//)
      WRITE(6,896)A0
 896  FORMAT(' A0= ',F15.5)
      WRITE(6,895)B0
 895  FORMAT(' B0= ',F15.5)
      WRITE(6,894)E0
 894  FORMAT(' S.D.(A0)= ',F15.5)
      WRITE(6,893)D0
 893  FORMAT(' S.D.(B0)= ',F15.5)
      WRITE(6,892)R5
 892  FORMAT(' CORRELATION COEFFT.= ',F8.6///)
 873  CONTINUE
      IF(L1.EQ.2)GOTO 881
      H1      =      A0/1000.
      EH1     =      E0/1000.
      S1      =      -B0
      ES1     =      D0
      DO I=1,N
      PC(I)   =      P2(I)/P0
      ENDDO
      IF(BRIEF.EQ.1)GOTO 872
      PRINT*,'LS FOR P2'
      PRINT*,'*********'
      PRINT*,'     '
 872  CONTINUE
      CALL LS(N,A0,B0,E0,D0,R5)
      IF(L1.EQ.1)GOTO 883
 881  H3      =      A0/1000.
      EH3     =      E0/1000.
      S3      =      -B0
      ES3     =      D0
      H2      =      H3-2.*H1
      S2      =      S3-2.*S1
      EH2     =      SQRT(EH3*EH3+4.*EH1*EH1)
      ES2     =      SQRT(ES3*ES3+4.*ES1*ES1)
```

```
      PRINT*,'Diffusion parameters = ',D12,D24,OPS1,OPS2
      PRINT*,'_____________________________________________________'
      PRINT*,'PT constants: A=',A,'B= ',B
      PRINT*,'_____________________________________________________'
      PRINT*,'H1= ',H1,'  +/-',EH1
      PRINT*,'S1= ',S1,'  +/-',ES1
      PRINT*,'********************'
      PRINT*,'H2= ',H2,'  +/-',EH2
      PRINT*,'S2= ',S2,'  +/-',ES2
      PRINT*,'********************'
      END
C
      SUBROUTINE LS(N,A0,B0,E0,D0,R5)
C *** LEAST SQUARES ON STRAIGHT LINE IN FORM Y=BOX+A0.
C *** GIVES GRADIENT(B0), INTERCEPT(A0), THEIR
C *** STANDARD DEVIATIONS AND A CORRELATION COEFFICIENT
      DIMENSION X1(200),Y1(200)
      COMMON/LS/ TK(200),PC(200),R
      DO 10 I=1,N
      X1(I)=TK(I)
      Y1(I)=-R*X1(I)*ALOG(PC(I))
  10  CONTINUE
      S1=0.
      S2=0.
      S3=0.
      S4=0.
      S5=0.
      S6=0.
      S7=0.
      DO 30 I=1,N
      S0=X1(I)
      S1=S1+S0
      S2=Y1(I)
      S3=S3+S2
      S4=X1(I)*Y1(I)
      S5=S5+S4
      S6=X1(I)*X1(I)
      S7=S7+S6
  30  CONTINUE
      FN=FLOAT(N)
      C0=S1*S1-FN*S7
      B0=(S3*S1-FN*S5)/C0
      A0=(S5*S1-S3*S7)/C0
      X0=S1/FN
      Y0=S3/FN
      S8=0.
      S9=0.
      T0=0.
      T1=0.
      T2=0.
```

```
      T3=0.
      T4=0.
      T5=0.
      DO 40 I=1,N
      S8=(X1(I)-X0)**2
      S9=S9+S8
      T0=(Y1(I)-B0*X1(I)-A0)**2
      T1=T1+T0
      T2=(Y1(I)-Y0)**2
      T3=T3+T2
      T4=(X1(I)-X0)*(Y1(I)-Y0)
      T5=T5+T4
 40   CONTINUE
      D0=SQRT(T1/((FN-2.)*S9))
      E0=SQRT(T1*S7/(FN*(FN-2.)*S9))
      R4=(B0**2)*S9/T3
      R3=SQRT(R4)
      R5=T5/SQRT(S9*T3)
      RETURN
      END
C
C*********************************************************************
C***   EVAPORATION OF MOLTEN ZINC CHLORIDE USING MEM RESULTS
C***   COUPLED WITH ABSOLUTE ZINC CHLORIDE VAPOUR PRESSURE
C***   MEASUREMENTS. EXACT TEMPERATURE RANGE USED BASED ON
C***   LITERATURE PRESSURE [ 360-705 C]
C
C              ZnCl2(c)        =       ZnCl2(g)        K1
C             2ZnCl2(g)        =       Zn2Cl4(g)       K2
C*********************************************************************
      END
```

```
      PROGRAM ZNSDS3G
C
C   MAIN PROGRAMMER P.J.GARDNER  JUNIOR PROGRAMMER P.PANG
C
C   MODIFIED PJG PROGRAM ZNSDS3G
C   RAW DATA OF ZINC SULPHIDE IN HYDROGEN IN FILE ZNSH2.EMF
C   ARE INITIALLY BROKEN DOWN INTO INDIVIDUAL SET OF EXPERIMENTS
C   AND RENAMED ZNSDS3G-.DAT WHERE -=A-Z.
      REAL K10(100),K11(100),K5(100)
C
C
C
C   ZNSDS3G= ZINC SULPHIDE DISSOCIATIVE SUBLIMATION. WILL DETERMINE
C   K10,& GAMMA CORRECTIONS GIVEN WDOT AND K11(T)- PJG NOTATION
C            N.B. INCONGRUENT SUBLIMATION!
C
C     ZNS(C)          =        ZN(G) + 0.5S2(G)     K10
C    H2(G) + 0.5S2(G)         =         H2S(G)              K11
C
C
C
       REAL D5(100),D9(100),D10(100),DELTA(100),TK(100)
       REAL WDOTE(100),P(100),TC(100),X(100),EMF(100),MLNW(100)
      REAL X1(100),Y1(100)
      INTEGER RN(100)
      REAL L2,M(20)
      CHARACTER*80 FILENM,HEADER(10)
      COMMON M,E5,E9,E10
      WRITE(6,*)'ENTER ZINC SULPHIDE/HYDROGEN DATA FILE e.g. ZNSDS3GA.DAT'
      READ(5,'(A80)')FILENM
      OPEN(UNIT=8,FILE=FILENM,STATUS='OLD')
C
C
C VALUES OF M(I) SET TO 100 ARE DUMMY ARGUMENTS REQD. TO
C EVALUATE REDUNDANT ELEMENTS IN THE ARRAY D(I,J) IN THE
C SUBROUTINE GAMMA
C
C
      M(1) =100
      M(2) =100
      M(3) =100
      M(4) =0.0020159
      M(5) =0.06537
      M(6) =100
      M(7) =100
      M(8) =0.097434
      M(9) =0.064128
      M(10)=0.03408
      N=0
      WRITE(6,*)'   '
```

```
      DO I=1,10
      READ(8,'(A80)')HEADER(I)
      WRITE(6,'(1X,A80)')HEADER(I)
      END DO
      DO II=1,100
      READ(8,*)RN(II),EMF(II),TC(II),MLNW(II),P(II)
      IF(RN(II).EQ.0)GOTO 9998
      WDOTE(II)=EXP(-MLNW(II))
C  TEMP. CALIBRATION CORN. FOLLOWS
       TK(II)=TC(II)+0.012*TC(II)-10.9 + 273.15
      P(II)=P(II)*101325.00/760.00
      N=N+1
      END DO
 9998  CONTINUE
      WRITE(6,*)'     '
      WRITE(6,*)'ENTER L2,R2 in METRES and b CORRECTION'
      READ(5,*)L2,R2,BETA
C  MINITAB OPTION
      WRITE(6,*)'    '
      WRITE(6,*)'DO YOU REQUIRE PROCESSED DATA TK(I) AND R*TK(I)*LOG(K10)'
      WRITE(6,*)'ENTER 1 FOR YES OR 2 FOR NO'
      READ(5,*)L
      IF(L.EQ.1)THEN
      OPEN(UNIT=9,FILE='ZNSDS3G.OUT',STATUS='NEW')
      WRITE(6,*)'   '
      WRITE(6,*)'MINITAB DATA STORED ON FILE ZNSDS3G.OUT'
      ENDIF
C
C     5=ZN(G)    7=ZN(L)     8=ZNS(C)      9=S2(G)
C     10=H2S(G)     4=H2(G)
C
      PI=4.00*ATAN(1.000)
      R=8.314300
      PO=101325.00
      J1=1
      WRITE(6,992)J1
 992   FORMAT(' RESULTS SET NUMBER',I3)
       WRITE(6,991)
 991   FORMAT(' *************************',//)
       WRITE(6,995)
 995   FORMAT(X,' TEMP/C    TEMP/K      K10    DELTA       GA5',
     +'      GA9       GA10     K')
       WRITE(6,996)
 996   FORMAT(X,'**********************************************',
     +'******************************')
      DO 50 I=1,N
      TO=TK(I)/273.1500
      D5(I)=81.09E-6*TO**1.539
       D9(I)=4.89E-5*TO**1.73200
      D10(I)=5.88E-5*TO**1.68700
```

```
C HOLD INITIAL VALUES OF D
      D05=D5(I)
      D09=D9(I)
      D010=D10(I)
       W=PI*R2*R2*M(8)/(R*TK(I)*L2*BETA)
       X(I)=WDOTE(I)/W
       T5=1.
       T9=1.
       T10=1.
       K=0
 70     K=K+1
        E5=X(I)/(D5(I)*P(I))
        E9=X(I)/(D9(I)*P(I))
       E10=X(I)/(D10(I)*P(I))
C
C  E=XI, THE TRANSPORT FUNCTION
C  XI=XIBAR*F(DELTA)=XIBAR(approx), AS DELTA>>1
C
       CALL GAMMA(GA5,GA9,GA10)
       IF ((ABS((GA5-T5)/T5).LE..0001).AND.(ABS((GA9-T9)/T9).LE..0001)
     +.AND.(ABS((GA10-T10)/T10).LE..0001))THEN
      K11(I)=EXP(90333./(R*TK(I))-49.3/R)
        K5(I)=EXP(-126733.00/(R*TK(I))-24.02500*LOG10(TK(I))/
     +R+181.0900/R)
        PZN=P0*K5(I)
       B=K11(I)*D10(I)*P(I)/(D9(I)*P0)**0.500
       DELTA(I)=B*B/X(I)
       E=D5(I)*D9(I)**0.500*P0**1.500
       K10(I)=X(I)**2.00/(E*B)
        WRITE(6,998)TC(I),TK(I),K10(I),DELTA(I),GA5,GA9,GA10,K
 998    FORMAT(X,2(F7.2,XX),2(E9.4,XX),3(F7.4,XX),I3)
       ELSE
               T5=GA5
               T9=GA9
               T10=GA10
C  UPDATE DIFF. COEFFTS.
      D5(I)=D05/T5
      D9(I)=D09/T9
      D10(I)=D010/T10
               GOTO 70
       END IF
 50     CONTINUE
C
C *** LEAST SQUARES ON STRAIGHT LINE IN FORM Y=BOX+A0.
C *** GIVES GRADIENT(B0), INTERCEPT(A0), THEIR
C *** STANDARD DEVIATIONS AND A CORRELATION COEFFICIENT
       DO 20 I=1,N
       X1(I)=TK(I)
       Y1(I)=-R*X1(I)*LOG(K10(I))
       IF(L.EQ.1)THEN
        WRITE(9,*)TK(I),Y1(I)
        ENDIF
 20     CONTINUE
       S1=0
       S2=0
       S3=0
       S4=0
       S5=0
       S6=0
       S7=0
       DO 30 I=1,N
       S0=X1(I)
       S1=S1+S0
       S2=Y1(I)
       S3=S3+S2
       S4=X1(I)*Y1(I)
       S5=S5+S4
       S6=X1(I)*X1(I)
       S7=S7+S6
 30    CONTINUE
       C=S1*S1-N*S7
       B0=(S3*S1-N*S5)/C
       A0=(S5*S1-S3*S7)/C
       X0=S1/N
       Y0=S3/N
       S8=0
       S9=0
       T0=0
       T1=0
       T2=0
       T3=0
       DO 40 I=1,N
       S8=(X1(I)-X0)**2
       S9=S9+S8
       T0=(Y1(I)-B0*X1(I)-A0)**2
       T1=T1+T0
       T2=(Y1(I)-Y0)**2
       T3=T3+T2
 40    CONTINUE
       D0=SQRT(T1/((N-2.)*S9))
       E0=SQRT(T1*S7/(N*(N-2.)*S9))
       R4=(B0**2)*S9/T3
       R3=SQRT(R4)
        WRITE(6,890)
 890     FORMAT(//,X,'IN FOLLOWING LS ANALYSIS,Y = DELTA(G) AND X =T/K')
        WRITE(6,889)
 889     FORMAT(X,'****************************************************')
        WRITE(6,891)
 891   FORMAT(' LEAST SQUARES ANALYSIS: Y=BOX+A0 '/
     +' ----------------------------------',//)
```

```
      WRITE(6,896)A0
 896  FORMAT(' A0= ',F15.5)
      WRITE(6,895)B0
 895  FORMAT(' B0= ',F15.5)
      WRITE(6,894)E0
 894  FORMAT(' S.D.(A0)= ',F15.5)
      WRITE(6,893)D0
 893  FORMAT(' S.D.(B0)= ',F15.5)
      WRITE(6,892)R3
 892  FORMAT(' CORRELATION COEFFT.= ',F8.6///)
       STOP
       END
       SUBROUTINE GAMMA(GA5,GA9,GA10)
       DIMENSION D(20,20)
       REAL M(20)
       COMMON M,E5,E9,E10
       DO 80 I=1,10
       DO 60 J=1,10
       D(I,J)=SQRT(M(J)/M(I))-1.
 60     CONTINUE
 80     CONTINUE
       J9J=0
       J10J=1.
       J5J=1.
C
C   JIJ MEANS ji/J - FOR THIS SYSTEM JIJ=F(DELTA) AND SINCE
C   DELTA IS SO LARGE, ALL JIJ MAY BE APPROXIMATED AS ABOVE
C
       B5=0.5*(D(4,9)*D(5,9)*J9J+D(4,10)*D(5,10)*J10J-1.)
       B9=0.5*(D(4,5)*D(9,5)*J5J+D(4,10)*D(9,10)*J10J-1.)
       B10=0.5*(D(4,5)*D(10,5)*J5J+D(4,9)*D(10,9)*J9J-1.)
       GA5=1.+B5*E5
       GA9=1.+B9*E9
       GA10=1.+B10*E10
       RETURN
       END
```

```
           PROGRAM ZNSHCL10
C
C     PROGRAMMER  P.PANG
C
C   NOTATION FOR EQUILIBRIUM CONSTANTS AND DIFFUSION COEFFICIENTS
C   AS DESIGNATED BY P.PANG AND P.J.GARDNER SEE DOCUMENTATION.
C
C   MEM TRANSPORT REACTION CONSIDERED:
C      ZnS(c)  +  2HCl(g)   =   ZnCl2(g)  +   H2S(g)           K12
C                2ZnCl2(g) =    Zn2Cl4(g)                      K2
C                 ZnS(g)   =    Zn(g)      + 1/2 S2(g)         K10
C      H2(g)   + 1/2 S2(g)  =   H2S(g)                         K11
C
C   TEMPERATURE RANGE 750-1170C
C
C   FLUX NOTATION    BETA     =    J(Zn2Cl4)/J(ZnCl2)
C                    DELTA    =        J(Zn)/J(S2)
C                    THETA    =        J(H2)/J(H2S)
C                   GAMMA    =    DELTA - 2*THETA - 2
C
C   NOTE 1020C TRANSION OF ZINC BLENDE INTO WURTZITE
C   MAYBE APPLIED
C
C   EQUILIBRIA NOT CONSIDERED IN MEM TRANSPORT
C      Zn(g)   +  2HCl(g)   =   ZnCl2(g)                       K**
C      ZnCl2(g)+   H2(g)    =   Zn(g)      +  2HCl(g)          K3
C                  HCl(g)   =   1/2 H2(g) + 1/2 Cl2(g)         K**
C   but first two reactions taken care of in K12,K2,K10,K11
C   and HCl is stable over the temperature range.
C
C***MULTICOMPONENT DIFFUSION APPIELD(MCD)
C
C   DATA ARE COLLECTED FROM FILE ZNSHCL**.EMF
C   RESULTS ARE DUMPED ONTO FILE ZNSHCL8.OUT
C
C   NAG11/LIB ROUTINE CO2AEF SOLVES ALL POSITIVE ROOTS OF A REAL
C   POLYNOMINAL EQUATION USING THE METHOD OF GRANTS AND HITCHINS.
C
C
      DOUBLE PRECISION L2,RD2,BETACOR,EPSILON,R,PO,CAREA,EMF,TC,MLNW,P,DEL
      DOUBLE PRECISION WDOTE,TK,DA1,DA2.DA3,DA4.DA5,DA9,DA10
      DOUBLE PRECISION XXX,NX,DAA1,DAA2,DAA3,DAA4,DAA5,DAA9,DAA10
      DOUBLE PRECISION K2,K10,K11,K12,K12ESTD,G12ESTD,K14,G14,GAMMA,C,BETA
      DOUBLE PRECISION RE(4),XZ(4),YZ(4),PI,TOL,ZZ,X01AAF,X02AAF
      DOUBLE PRECISION ONE,P1,P15,ZERO,A1P1,CORRN
      DOUBLE PRECISION OMEGA,AAAAA,BBBBB,CCCCC,DDDDD,ZZZZZ,BOX
C
      DOUBLE PRECISION M(20),THI,AAAA,DDDD,EEEE,ZZZZ
      DOUBLE PRECISION TA1 ,TA2 ,TA3 ,TA4 ,TA5 ,TA9 ,TA10
      DOUBLE PRECISION EA1 ,EA2 ,EA3 ,EA4 ,EA5 ,EA9 ,EA10
      DOUBLE PRECISION MCD1,MCD2,MCD3,MCD4,MCD5,MCD9,MCD10
      DOUBLE PRECISION J1J,J2J,J3J,J4J,J5J,J6J,J7J,J8J,J9J,J10J
      DOUBLE PRECISION E1,E2,E3,E4,E5,E9,E10
      DOUBLE PRECISION PA1,PA2,PA3,PA4,PA5,PA9,PA10
C
      DOUBLE PRECISION D(20,20),A(10),B(10)
      INTEGER          RN,I,II,COUNT,N,NOF,T,IFAIL,NN,K,KMCD,III,JJJ
      CHARACTER*80     FILENM,HEADER(10),LINE
      CHARACTER*1      YN,Y,ZZZ
      COMMON MCD1,MCD2,MCD3,MCD4,MCD5,MCD9,MCD10,
     +EA1,EA2,EA3,EA4,EA5,EA9,EA10,
     +J1J,J2J,J3J,J4J,J5J,J8J,J9J,J10J
C
      DATA ONE/1.0D0/,P1/0.1D0/,P15/0.15D0/,ZERO /0.0D0/,A1P1/1.1D0/
C
 9960 FORMAT(' ENTER DATA FILE FOR ZNS(g) + HCl(g):  '$)
 9975 FORMAT(1X,I3,2X,F8.2,5(2X,G9.4),2X,G8.2)
 9978 FORMAT(1X,I3,F8.2,7(2X,F6.4),2X,I2)
 9979  FORMAT(1X,I3,F8.2,7(2X,G10.3))
 9980 FORMAT( '  ERROR NUMBER ',I4)
 9985 FORMAT( '  PROGRAM FAILS POLY ORDER ',I4)
 9990  FORMAT( ' ************************************
     +*****************************************',A1)
C
C
C     SPECIES PRESENT
C     ZnCl2         1     ZnS          8
C     Cl2           2     S2           9
C      HCl           3     H2S         10
C     H2            4     Ar          11
C     Zn            5
C
C
C     MOLECULAR WEIGHT  M(*) kg/mol.
      M(1) = 136.276D-3
      M(2) =  70.906D-3
      M(3) =  36.461D-3
      M(4) =   2.016D-3
      M(5) =  65.370D-3
      M(6) = 100.000D-3
      M(7) = 100.000D-3
      M(8) = 100.000D-3
      M(9) =  64.128D-3
      M(10)=  33.072D-3
      M(11)=  39.948D-3
C
C     CALLING RAW DATA FILE
      YN    = 'Y'
      ZZ    = 'X'
      TYPE 9960
```

```
      READ(5,'(A80)')FILENM
      OPEN(UNIT=8 ,FILE=FILENM       ,STATUS='OLD')
      OPEN(UNIT=9 ,FILE='ZNSHCL8.OUT',STATUS='NEW')
      OPEN(UNIT=10,FILE='ZNSHCL8.PRE',STATUS='NEW')
      OPEN(UNIT=11,FILE='ZNSHCL8.EXI',STATUS='NEW')
      WRITE(6,*)'  '
    9 DO I  = 1,10
              READ(8,'(A80)',END=9999)HEADER(I)
              WRITE(6,'(1X,A80)')HEADER(I)
      END DO
      WRITE(6,*)' '
C
   18 WRITE(6,*)'ENTER L2,R2,BETACOR,EPSILON IN SI UNITS'
      READ(5,*)L2,RD2,BETACOR,EPSILON
      WRITE(6,*)' '
      R     = 8.3142D0
      PO    = 101325.0D0
      CAREA = 4.00D0*DATAN(1.00D0)*(RD2**2.0D0)
      WRITE(6,*)' '
      WRITE(6,*)' G10(alpha) = 376746.0 -191.9T  G10(beta) = 374174.0
     +- 190.4T'
      WRITE(6,*)' '
      WRITE(6,*) ' RUN  TK     MCD1    MCD2    MCD3    MCD4
     +   MCD5    MCD9    MCD10    K  '
C
C     WRITE(9,*) ' RUN  TK       XZ(I)   DELTA
C    +BETA     K12EXP   K12ESTD ((EXP-ESTD))/ESTD)**2'
C
C     WRITE(10,*)' RUN  TK     P1      P2      P3      P4
C    +   P5      P9      P10      K  '
C
C     WRITE(11,*)' RUN  TK     E1      E2      E3      E4
C    +   E5      E9      E10      K  '
      WRITE(6, 9990)ZZZ
C     WRITE(9, 9990)ZZZZ
C     WRITE(10,9990)ZZZZ
C     WRITE(11,9990)ZZZZ
   19         READ(8,*)RN,EMF,TC,MLNW,P
              IF (RN .EQ. 0) GOTO 9999
C
              WDOTE      = DEXP(-MLNW)
C             TK         = 273.15D0 + TC
              TK         = - 10.9D0 + 0.012D0*TC + 273.15D0 + TC
              P          = P*101325.0D0/760.0D0
C
C             BINARY DIFFUSION COEFFICIENTS IN ARGON
              DA1        =  8.624D-6*((TK/273.15D0)**1.760D0)
              DA2        = 10.639D-6*((TK/273.15D0)**1.683D0)
              DA3        = 15.475D-6*((TK/273.15D0)**1.686D0)
              DA4        = 73.026D-6*((TK/273.15D0)**1.741D0)
              DA5        = 12.420D-6*((TK/273.15D0)**1.793D0)
              DA9        =  8.608D-6*((TK/273.15D0)**1.720D0)
              DA10       = 14.800D-6*((TK/273.15D0)**1.682D0)
C
C             HOLDING CURRENT BINARY DIFFUSION COEFFICIENTS
              DAA1       = DA1
              DAA2       = DA2
              DAA3       = DA3
              DAA4       = DA4
              DAA5       = DA5
              DAA9       = DA9
              DAA10      = DA10
C
C             MULTICOMPONENT DIFFISION CORRECTION T - TEST
              TA1        = 1.0D0
              TA2        = 1.0D0
              TA3        = 1.0D0
              TA4        = 1.0D0
              TA5        = 1.0D0
              TA9        = 1.0D0
              TA10       = 1.0D0
C
C             COUNTING NUMBER OF TIMES MCD CORR APPLIED K
              K          = 0
C
              XXX        = WDOTE*R*TK*L2*BETACOR/(CAREA*97.434D-3)
C
C             SET UP EQUILIBRIUM CONSTANT FROM RELIABLE SOURCES
C             RHBNC RESULTS: K2 AND K10.
C             JANAF TABLES : K11.
C             PJG CALC     : G12ESTD
              G12ESTD    = 94111.0D0 - 17.13D0*TK*DLOG10(TK) + 7.05D0*TK
              G14        = 93800.0D0 + 9.44D0*TK*DLOG10(TK) - 38.60D0*TK
              K14        = DEXP(-G14/(R*TK))
              IF (TK .GT. 1293.0D0) THEN
              K10        = DEXP(-376746.0D0/(R*TK) + (191.9D0/R))
C             K10        = DEXP(-364543.0D0/(R*TK) + (182.9D0/R))
              ELSE
              K10        = DEXP(-374174.0D0/(R*TK) + (190.4D0/R))
              ENDIF
              K11        = DEXP(  90333.0D0/(R*TK) - (49.30D0/R))
              K12ESTD    = DEXP(-G12ESTD/(R*TK))
C
C
C              NAG11/LIB C02AEF SUBPROGRAM
              COUNT      = 1
              KMCD       = 0
              PI         = P1*X01AAF(P1)
              TOL        = X02AAF(P1)
   20         T          = 0
```

```
              XZ(1)      = P15
              YZ(1)      = ZERO
              IFAIL      = 1
              N          = 4
              NN         = 3
              IF (COUNT .EQ. 0 .AND. KMCD .EQ.0) GOTO 19
              COUNT      = 0
              K          = K + 1
C
C             E=XIBAR,THE TRANSPORT FUNCTION WITHOUT *J/J8 TERM
              EA1        = XXX/(DA1*P)
              EA2        = XXX/(DA2*P)
              EA3        = XXX/(DA3*P)
              EA4        = XXX/(DA4*P)
              EA5        = XXX/(DA5*P)
              EA9        = XXX/(DA9*P)
              EA10       = XXX/(DA10*P)
C
C
              AAAA       = EA9*EA4*(K11**2.0D0)
              DDDD       = (EA10**2.0D0)*101325.0D0
              EEEE       = K14*EA1*EA10/(K10*K11*EA2*EA4)
              ZZZZ       = EA9*(EA4**3.0D0)*K10*(K11**3.0D0)
     .                     /((EA10**3.0D0)*EA5)
C
C             CUBIC EQUATION SOLVING WHERE XZ(I)=THETA
              RE(1)      = AAAA + DDDD*ZZZZ
              RE(2)      = DDDD*EEEE*ZZZZ
              RE(3)      = -(AAAA*EEEE + 2.0D0*DDDD)
              RE(4)      = -2.0D0*DDDD
 40           NOF        = N - 1
              CALL C02AEF(RE,N,XZ,YZ,TOL,IFAIL)
              IF (IFAIL .NE. 0) GOTO 120
 60           I          = NOF + 1
 80           I          = I - 1
              IF (I .LT. N) GOTO 100
              ZZ         = DSQRT(XZ(I)**2.0D0 + YZ(I)**2.0D0)
C
C      ONLY POSITIVE XZ(I)-THETA  IS ALLOWED
       IF (XZ(I) .GT. 0.0D0) THEN
       DELTA = (XZ(I)**3.0D0)*ZZZZ
       AAAAA = EA9*EA4*(K11**2.0D0)*(XZ(I)**3.0D0)
       BBBBB = (EA10**2.0D0)*101325.0D0*(-DELTA+2.0D0+2.0D0*XZ(I))
       CCCCC = EA9*EA4*(K11**2.0D0)*(XZ(I)**2.0D0)
       DDDDD = (EA10**2.0D0)*DELTA*101325.0D0
       OMEGA = (AAAAA-BBBBB)/(CCCCC-DDDDD)
       THI   = 1.0D0 + OMEGA - 2.0D0*(1.0D0+OMEGA) + (1.0D0+OMEGA)
     ./(1.0D0+XZ(I))  + XZ(I)*(1.0D0+OMEGA)/(1.0D0+XZ(I))
     .+      (XZ(I)-OMEGA)/((1.0D0+XZ(I))*(2.0D0-DELTA))
     .+DELTA*(XZ(I)-OMEGA)/((1.0D0+XZ(I))*(2.0D0-DELTA))
```

```
     .+(2.0D0-DELTA+2.0D0*XZ(I)-OMEGA*DELTA)/((1.0D0+XZ(I))
     .*(2.0D0-DELTA))
C
C      JIJ MEANS FLUX Ji/J
       J1J   = 1.0D0/THI
       J2J   = OMEGA/THI
       J3J   = -2.0D0*(1.0D0 + OMEGA)/THI
       J4J   = XZ(I)*(1.0D0 + OMEGA)/(THI*(XZ(I)+1.0D0))
       J5J   =DELTA*(XZ(I)-OMEGA)/((1.0D0+XZ(I))*(2.0D0-DELTA)*THI)
       J8J   = (2.0D0 - DELTA + 2.0D0*XZ(I) - OMEGA*DELTA)
     .         /((1.0D0+XZ(I))*(2.0D0-DELTA)*THI)
       J9J   = (XZ(I)-OMEGA)/((1.0D0+XZ(I))*(2.0D0-DELTA)*THI)
       J10J  = (1.0D0 + OMEGA)/((XZ(I)+1.0D0)*THI)
C
C
C      TESTING CORRELATION OF MCD* WITH T*
       CALL MCDCORR(M,EPSILON)
       IF( ABS ((MCD1 - TA1)/TA1 .LE. 0.0001) .AND.
     +       ABS ((MCD2 - TA2)/TA2 .LE. 0.0001) .AND.
     +       ABS ((MCD3 - TA3)/TA3 .LE. 0.0001) .AND.
     +       ABS ((MCD4 - TA4)/TA4 .LE. 0.0001) .AND.
     +       ABS ((MCD5 - TA5)/TA5 .LE. 0.0001) .AND.
     +       ABS ((MCD9 - TA9)/TA9 .LE. 0.0001) .AND.
     +       ABS ((MCD10-TA10)/TA10.LE. 0.0001))THEN
C
C*******CALCULATING K12 FROM EXPT. RESULTS
       KMCD  = 0
C      PRESSURE OF GASES IN mmHg
       BOX   = 2.0D0 - DELTA + 2.0D0*XZ(I) - OMEGA*DELTA
       PA1   = (1.0D0+XZ(I))*(2.0D0-DELTA)*EA1/BOX
       PA2   = OMEGA*(1.0D0+XZ(I))*(2.0D0-DELTA)*EA2/BOX
       PA3   =(EPSILON*P*BOX - 2.0D0*(1.0D0+OMEGA)*(1.0D0+XZ(I))
     +         *(2.0D0-DELTA)*EA3)/BOX
       PA4   = XZ(I)*(1.0D0+OMEGA)*(2.0D0-DELTA)*EA4/BOX
       PA5   = DELTA*(XZ(I)-OMEGA)*EA5/BOX
       PA9   = (XZ(I)-OMEGA)*EA9/BOX
       PA10  = (1.0D0+OMEGA)*(2.0D0-DELTA)*EA10/BOX
       K12   = PA10*PA1/(PA3**2.0D0)
       PA1   = PA1*760.0D0/101325.0D0
       PA2   = PA2*760.0D0/101325.0D0
       PA3   = PA3*760.0D0/101325.0D0
       PA4   = PA4*760.0D0/101325.0D0
       PA5   = PA5*760.0D0/101325.0D0
       PA9   = PA9*760.0D0/101325.0D0
       PA10  =PA10*760.0D0/101325.0D0
C      XI
       E1    = EA1 /J8J
       E2    = EA2 /J8J
       E3    = EA3 /J8J
       E4    = EA4 /J8J
```

```
      E5    = EA5 /J8J
      E9    = EA9 /J8J
      E10   = EA10/J8J
      CORRN = ((K12-K12ESTD)/K12ESTD)**2.0D0
      WRITE(9, 9975)RN,TK,XZ(I),DELTA,OMEGA,K12,K12ESTD,CORRN
      WRITE(6, 9978)RN,TK,MCD1,MCD2,MCD3,MCD4,MCD5,MCD9,MCD10,K
      WRITE(10,9979)RN,TK,PA1,PA2,PA3,PA4,PA5,PA9,PA10
      WRITE(11,9978)RN,TK,E1,E2,E3,E4,E5,E9,E10
C
      ELSE
C
C     APPLYING MCD CORRECTION
      TA1   = MCD1
      TA2   = MCD2
      TA3   = MCD3
      TA4   = MCD4
      TA5   = MCD5
      TA9   = MCD9
      TA10  = MCD10
      DA1   = DAA1/TA1
      DA2   = DAA2/TA2
      DA3   = DAA3/TA3
      DA4   = DAA4/TA4
      DA5   = DAA5/TA5
      DA9   = DAA9/TA9
      DA10  = DAA10/TA10
      KMCD  = 1
      ENDIF
              ENDIF
              GOTO 80
 100          IF (N .NE. 1) GOTO 40
              GOTO 20
 120          WRITE(6,9980)IFAIL
              IF (T .NE. 20 .AND. IFAIL .EQ. 2) GOTO 140
              N          = N - 1
              WRITE(6,9985)N
              GOTO 20
 140          T          = T + 1
              XZ(1)=XZ(1)*A1P1*COS(FLOAT(T)*PI)-YZ(1)*A1P1*SIN(FLOAT(T)*PI
              YZ(1)=XZ(1)*A1P1*SIN(FLOAT(T)*PI)+YZ(1)*A1P1*COS(FLOAT(T)*PI
              GOTO 60
 9999 STOP' DATA STORED ON FILE ZNSHCL8.OUT,ZNSHCL8.PRE,ZNSHCL8.EXI'
      END
C
C     MCD "GAMMA" CORRECTION
      SUBROUTINE MCDCORR(M,EPSILON)
      DOUBLE PRECISION A(10),B(10),M(20),D(20,20)
      DOUBLE PRECISION MCD1,MCD2,MCD3,MCD4,MCD5,MCD9,MCD10
      DOUBLE PRECISION EA1,EA2,EA3,EA4,EA5,EA9,EA10,EPSILON
      DOUBLE PRECISION J1J,J2J,J3J,J4J,J5J,J6J,J7J,J8J,J9J,J10J
```

```
       INTEGER III,JJJ
       COMMON MCD1,MCD2,MCD3,MCD4,MCD5,MCD9,MCD10,
     +EA1,EA2,EA3,EA4,EA5,EA9,EA10,
     +J1J,J2J,J3J,J4J,J5J,J8J,J9J,J10J
C
C      USING GRAHAM'S LAW OF SCALING THROUGHOUT
C      i.e. Dik/Djk = (Mj/Mi)**0.5
C      or   D(i,j)  = [Dik/Djk - 1]
       DO 999   III = 1,11
       DO 888   JJJ = 1,11
       D(III,JJJ)   = DSQRT(M(JJJ)/M(III))-1.0D0
 888   CONTINUE
 999   CONTINUE
C      MULTICOMPONENT DIFFUSION (MCD) "GAMMA CORRECTION"
C      FOR MINORITY SPECIES IN ARGON GAS
C       FIRST TERM A(**)
       A(1)   = D(11,3)
       A(2)   = D(11,3)
       A(4)   = D(11,3)
       A(5)   = D(11,3)
       A(9)   = D(11,3)
       A(10)  = D(11,3)
C      SECOND TERM B(**)
       B(1)=(D(11,2)*D(1,2)*J2J+D(11,4)*D(1,4)*J4J+D(11,5)*D(1,5)*J5J
     ++D(11,9)*D(1,9)*J9J
     ++D(11,10)*D(1,10)*J10J+D(11,3)*D(1,3)*J3J-1.0D0)*0.50D0
C
       B(2)=(D(11,1)*D(2,1)*J1J+D(11,4)*D(2,4)*J4J+D(11,5)*D(2,5)*J5J
     ++D(11,9)*D(2,9)*J9J+D(11,10)*D(2,10)*J10J+D(11,3)*D(2,3)*J3J
     +-1.0D0)*0.50D0
C
       B(4)   = (D(11,1) *D(4,1) *J1J  + D(11,2)*D(4,2)*J2J
     +            + D(11,5) *D(4,5) *J5J  + D(11,9)*D(4,9)*J9J
     ++ D(11,10)*D(4,10)*J10J + D(11,3)*D(4,3)*J3J - 1.0D0)*0.5D0
C
       B(5)   = (D(11,1) *D(5,1) *J1J  + D(11,2)*D(5,2)*J2J
     +            + D(11,4) *D(5,4) *J4J  + D(11,9)*D(5,9)*J9J
     ++ D(11,10)*D(5,10)*J10J + D(11,3)*D(5,3)*J3J - 1.0D0)*0.5D0
C
       B(9)   = (D(11,1) *D(9,1) *J1J  + D(11,2)*D(9,2)*J2J
     +            + D(11,4) *D(9,4) *J4J  + D(11,5)*D(9,5)*J5J
     ++ D(11,10)*D(9,10)*J10J + D(11,3)*D(9,3)*J3J - 1.0D0)*0.5D0
C
       B(10)  = (D(11,1) *D(10,1)*J1J  + D(11,2)*D(10,2)*J2J
     +            + D(11,4) *D(10,4)*J4J  + D(11,5)*D(10,5)*J5J
     ++ D(11,9) *D(10,9)*J9J  + D(11,3)*D(10,3)*J3J -1.0D0)*0.5D0
C
C      CORRECTION FOR TRANSPORTING SPECIES HCL(g) in ARGON(g)
C      FIRST TERM
       A(3)   = -D(11,1)*J1J - D(11,2)*J2J - D(11,4)*J4J
```

```
     +-D(11,5)*J5J - D(11,9)*J9J - D(11,10)*J10J-1.0D0/ J3J
C       SECOND TERM
        B(3)    = (D(11,1)*D(3,1)*J1J + D(11,2)*D(3,2)*J2J
     +               +D(11,4)*D(3,4)*J4J + D(11,5)*D(3,5)*J5J
     ++D(11,9)*D(3,9)*J9J + D(11,10)*D(3,10)*J10J - 1.0D0)*0.5D0
C
        MCD1    = 1.0D0 + A(1)*EPSILON + B(1)*EA1/J8J
        MCD2    = 1.0D0 + A(2)*EPSILON + B(2)*EA2/J8J
        MCD3    = 1.0D0 + A(3)*EPSILON + B(3)*EA3/J8J
        MCD4    = 1.0D0 + A(4)*EPSILON + B(4)*EA4/J8J
        MCD5    = 1.0D0 + A(5)*EPSILON + B(5)*EA5/J8J
        MCD9    = 1.0D0 + A(9)*EPSILON + B(9)*EA9/J8J
        MCD10   = 1.0D0 +A(10)*EPSILON +B(10)*EA10/J8J
        RETURN
        END
```

```
      PROGRAM ZNCL22NH3A
C
C     PROGRAMMER  P.PANG
C
C     EQUILIBRIUM OF ZINC DIAMMINE CHLORIDE IN ARGON.
C
C     Temperature Range 150C-318C. Below melting point of
C     zinc chloride the equilibrium of zinc diammine chloride
C     is as follows:
C     ZnCl2.2NH3 (c)    =   ZnCl2NH3(l) +    NH3 (g)        K5
C     ZnCl2.2NH3 (c)    =   ZnCl2 (c)    +   2NH3 (g)        K7
C
C     The rate of weight loss due to sublimination of zinc chloride
C     is considered to negilible below its melting point for MEM work.
C
C...  Program calculates equilibrium constant K3 as a function of
C     temperature. Data is stored on ZNCL22NH3.OUT: 1   WDOT / Kg/s
C                                                   2   P3   / N/m2
C                                                   3   K5
C                                                   4   K7
C                                                   5   TK
C                                                   6   XI
C
      REAL L2,R2,PI,R,PO
      REAL RN(200),EMF(200),TK(200),MLNW(200),P(200),WDOTE(200)
      REAL A,M3,D3,P3,K5,K7,XI
      INTEGER I,II
      CHARACTER*80 HEADER(100)
C
      OPEN(UNIT=7,FILE='ZNCL22NH3B.EMF',STATUS='OLD')
      OPEN(UNIT=8,FILE='ZNCL22NH3.OUT' ,STATUS='NEW')
C
      DO I = 1,10
      READ(7,'(A80)')HEADER(I)
      WRITE(6,'(1X,A80)')HEADER(I)
      END DO
C
      L2 = 1.8512E-2
      R2 = 0.0542E-2
      PO = 101325.0
      PI = 4.00*ATAN(1.000)
      A  = PI*R2*R2
      R  = 8.3142
      M3 =17.0306E-3
      WRITE(6,*)'                PRESSURE'
      WRITE(6,*)'WDOT / Kg/s  AM / N/M2      K5             K7
     .TK          XI'
      WRITE(6,*)'**************************************************
     .*******************'
C
      DO II= 1,200
      READ(7,*)RN(II),EMF(II),TK(II),MLNW(II),P(II)
      IF(RN(II) .EQ. 0)GOTO 999
C     IF(TK(II) .LT. 500.0)THEN
      IF(TK(II) .LT. 502.0 .AND. RN(II) .GE. 5)THEN
      WDOTE(II) = EXP(-MLNW(II))
      P(II)     = P(II)*PO/760.0
C OLD D3        = 1.8650E-5*((TK(II)/273.15)**1.8036)
      D3        = 1.8250E-5*((TK(II)/273.15)**1.8420)
      XI        = WDOTE(II)*R*TK(II)*L2/(D3*A*M3*P(II))
      P3        = P(II)*(1.0 - EXP(-XI))
      K5        = P3/PO
      K7        = (P3/PO)**2.0
      WRITE(8,'(2X,E10.4,3X,F9.2,3X,E10.4,3X,E10.4,3X,F6.2,3X,E9.3)')
     .WDOTE(II),P3,K5,K7, TK(II),XI
      WRITE(6,'(2X,E10.4,3X,F9.2,3X,E10.4,3X,E10.4,3X,F6.2,3X,E9.3)')
     .WDOTE(II),P3,K5,K7, TK(II),XI
      ENDIF
      END DO
C
 999  WRITE(6,*)' '
      WRITE(6,*)' DATA STORED ON FILE ZNCL22NH3.OUT : TK,P3,K5,K7,TK,XI'
      WRITE(6,*)' MINITAB EXECUTE ZNCL22NH3A.MTB'
      STOP
      END
```

```
MINITAB ROUTINE WRITTEN FOR MAIN PROGRAM ZNCL22NH3A.FOR
PROGRAMMER     P.PANG
*******************************************************
ECHO
NAME C1 'W10E10'
NAME C2 'A N/M2'
NAME C3 'K5'
NAME C4 'K7'
NAME C5 'TK'
NAME C6 'XI'
NAME C7 '^G5'
NAME C8 '^G7'
READ 'ZNCL22NH3.OUT'C1-C6
SORT  C5[C1-C4,C6] C5[C1-C4,C6]
LET   C1 = C1*1E10
PRINT C5,C1-C4,C6
LET C7 = -8.3142*C5*LOGE(C3)
LET C8 = -8.3142*C5*LOGE(C4)
PRINT C7,C8,C5
REGRESS C7 1 C5
PLOT C7 C5
REGRESS C8 1 C5
PLOT C8 C5
END
```

Appendix 4

MEM Raw Data Files

```
DATA FILE SERIES:ZNH2D.EMF
DIFFUSION COEFFICIENT DATA OF ZINC IN HYDROGEN.23/6/86.
FLOW OF HYDROGEN = 90cc/min. THERMOCOUPLE Pt:13%Rh/Pt.
No. OF DATA POINTS =56. CAHN R100 ELECTROBALANCE USED.
DIMENSIONS OF RE-ENTRANT CAPILLARY CHANNEL:
LENGTH L2     = 2.1008 +/- 0.0053cm.
RADIUS R2     = 0.0560 +/- 0.0010cm.
b CORRECTION = 1.000       INTERNAL PRESSURE 4.12mmHg.

RUN      EMF     -InW    PRESSURE
 2        7.074  19.7662  761.230
 3        7.074  19.7662  761.180  ROGUE RUN VALUES
 4        7.074  19.7636  761.140   1 7.074 19.7817 761.27
 5        7.074  19.7583  761.010   9 7.454 19.2751 760.91
 6        7.074  19.7609  761.060  26 8.514 17.9345 760.72
 7        7.074  19.7662  761.010  32 6.807 20.1089 760.27
 8        7.074  19.7609  760.970  52 3.610 WDOTE=.0Kg/sec
10        7.467  19.2601  760.850
11        7.464  19.2631  760.800
12        7.461  19.2631  760.740
13        7.461  19.2683  760.680
14        7.463  19.2683  760.620
15        7.715  18.9430  760.640
16        7.719  18.9395  760.660
17        7.719  18.9386  760.680
18        7.719  18.9395  760.700
19        7.718  18.9404  760.720
20        8.101  18.4599  760.720
21        8.105  18.4541  760.720
22        8.108  18.4502  760.720
23        8.109  18.4502  760.720
24        8.108  18.4483  760.720
25        8.107  18.4522  760.720
27        8.511  17.9297  760.720
28        8.512  17.9272  760.720
29        8.516  17.9247  760.720
30        8.516  17.9272  760.720
31        8.516  17.9223  760.720
33        6.816  20.1071  760.040
34        6.816  20.1071  759.800
35        6.821  20.0987  759.570
36        6.823  20.0987  759.340
37        6.824  20.0987  759.100
38        6.824  20.0987  758.870
39        6.458  20.6095  758.720
40        6.461  20.6146  758.820
41        6.462  20.6095  758.920
42        6.462  20.6062  759.020
43        6.460  20.6062  759.120
44        6.017  21.2737  759.190
```

```
45        6.017  21.2714  759.260
46        6.017  21.2835  759.330
47        5.338  22.3985  759.410
48        5.338  22.4097  759.480
49        5.338  22.4316  759.550
50        5.338  22.4531  759.620
51        3.610  26.4607  759.620
53        5.007  23.3089  764.620
54        5.006  23.0924  764.670
55        5.006  23.1162  766.270
56        5.006  23.1471  766.040
57        5.006  23.0411  765.800
58        4.586  23.9117  765.570
59        4.586  23.9916  766.870
60        4.586  23.9905  768.170
61        4.033  25.2719  768.170
0         0.000   0.0000    0.000
          mV     -In(Kg/s) mmHg
```

```
DATA FILE SERIES:ZNHEA.EMF
DIFFUSION COEFFICIENT DATA OF ZINC IN HELIUM. 15/7/86.
FLOW OF HELIUM = 90cc/min (calc.) THERMOCOUPLE Pt:13%Rh/Pt.
No. OF DATA POINTS =57. CAHN R100 ELECTROBALANCE USED.
DIMENSIONS OF RE-ENTRANT CAPILLARY CHANNEL:
LENGTH L2     = 2.1008 +/- 0.0053cm.
RADIUS R2     = 0.0560 +/- 0.0010cm.
b CORRECTION = 1.000        INTERNAL PRESSURE 5.53mmHg.

RUN      EMF     -InW    PRESSURE
 1       5.463  22.4616 772.230
 2       5.463  22.4616 772.230      I. MASS OF Zn 126mg.
 3       5.463  22.4721 772.230      F.   "  "  "  46mg.
 4       5.463  22.4679 772.230
 5       5.785  21.9016 772.230
 6       5.785  21.8905 772.490
 7       5.785  21.8849 772.760
 8       5.785  21.9181 773.030
 9       6.116  21.3662 772.890
10       6.116  21.3567 772.750
11       6.116  21.3471 772.610
12       6.116  21.3471 772.470
13       6.116  21.3535 772.330
14       6.116  21.3567 772.190
15       5.124  23.0562 772.060
16       5.124  23.0849 771.920
17       5.124  23.0860 771.780
18       6.458  20.8508 771.780
19       6.458  20.8490 771.780
20       6.458  20.8508 771.780
21       6.458  20.8473 771.780
22       6.458  20.8437 771.780
23       6.820  20.3168 771.780
24       6.820  20.3302 771.780
25       6.820  20.3258 771.780
26       6.820  20.3168 771.780
27       6.820  20.3168 771.780
28       7.198  19.8231 771.780
29       7.198  19.8157 771.780
30       7.198  19.8268 771.780
31       7.198  19.8194 771.780
32       7.198  19.8194 771.780
33       7.589  19.3168 771.380
34       7.589  19.3127 771.380
35       7.589  19.3208 771.380
36       7.589  19.3249 771.380
37       7.589  19.3370 771.380
38       7.981  18.8394 771.380
39       7.981  18.8368 771.380
40       7.981  18.7937 771.380

41       7.981  18.8525 771.380
42       7.981  18.8261 771.380
43       8.513  18.1645 771.380
44       8.513  18.1528 771.380
45       8.513  18.1548 771.380
46       8.513  18.1606 771.380
47       8.513  18.1664 771.380       WDOT LOW. RUN
48       8.513  18.1606 771.380       49-51,52-53,54-57
49       4.820  23.7470 771.380       POSSIBLE OXIDE LAYER OR
50       4.820  23.7517 771.380       KINETIC BARRIER EFFECT.
51       4.820  23.7517 771.380
52       4.491  24.5061 771.380
53       4.491  24.5219 771.380
54       4.491  24.7459 771.380
55       4.491  25.0402 771.380
56       4.491  24.9486 771.380
57       4.491  24.9381 771.380
0        0.000   0.0000   0.000
         mV     -In(Kg/s) mmHg
```

```
DATA FILE SERIES:ZNN2C.EMF
DIFFUSION COEFFICIENT DATA OF ZINC IN NITROGEN.30/6/86.
FLOW OF NITROGEN = 90cc/min. THERMOCOUPLE Pt:13%Rh/Pt.
No. OF DATA POINTS = 75. CAHN R100 ELECTROBALANCE USED.
DIMENSIONS OF RE-ENTRANT CAPILLARY CHANNEL:
LENGTH L2     = 2.1008 +/- 0.0053cm.
RADIUS R2     = 0.0560 +/- 0.0010cm.
b CORRECTION = 1.000      INTERNAL PRESSURE 5.79mmHg.

RUN      EMF      -InW    PRESSURE
 1       6.959  21.2421  773.04
 2       6.959  21.2094  773.04
 3       6.959  21.2240  773.04
 4       5.896  22.7255  773.15
 5       5.896  22.7603  773.26
 6       5.896  22.7774  773.37
 7       5.896  22.8254  773.48
 8       7.459  20.5817  773.59
 9       7.459  20.5771  773.59
10       7.459  20.5701  773.59
11       7.459  20.5771  773.59
12       7.459  20.5745  773.59
13       7.459  20.5745  773.59
14       7.974  19.9248  773.54
15       7.974  19.9214  773.54
16       7.974  19.9347  773.54
17       7.974  19.9248  773.54
18       7.974  19.9181  773.54
19       7.974  19.9181  773.54
20       7.974  19.9214  773.54
21       8.382  19.3990  773.54
22       8.382  19.3762  773.54
23       8.382  19.3839  773.54
24       8.382  19.3839  773.54
25       8.382  19.3952  773.54
26       8.382  19.3723  773.54
27       8.382  19.3800  773.54
28       8.382  19.3800  773.54
29       8.726  18.8832  773.54
30       8.726  18.8654  773.54
31       8.726  18.8730  773.54
32       8.726  18.8705  773.54
33       8.726  18.8730  773.54
34       8.726  18.8781  773.41
35       6.586  21.7396  773.28
36       6.586  21.7330  773.15
37       6.586  21.7412  773.02
38       6.586  21.7461  772.89
39       6.586  21.7330  772.76
40       6.586  21.7493  772.64
41       6.586  21.7396  772.51
42       6.586  21.7363  772.38
43       6.586  21.7232  772.25
44       6.586  21.7232  772.12
45       6.586  21.7396  771.99
46       6.241  22.2273  771.86
47       6.241  22.2353  771.75
48       6.241  22.2406  771.50
49       6.241  22.2406  771.26
50       6.241  22.2458  771.01
51       6.241  22.2537  770.77
52       6.241  22.2537  770.52
53       4.814  24.9084  770.28
54       4.814  24.7938  770.03
55       4.814  24.7001  769.79
56       4.814  24.8806  769.54
57       5.349  23.7534  769.17
58       5.349  23.6906  768.79
59       5.349  23.6844  768.42
60       5.349  23.7621  768.04
61       5.349  23.6688  767.67
62       5.349  23.6844  767.29
63       5.349  23.6998  766.92
64       5.349  23.7848  766.54
65       5.349  23.6875  766.17
66       5.349  23.6813  765.79
67       5.679  23.1642  766.14
68       5.679  23.1226  766.49
69       5.679  23.1484  766.84
70       5.679  23.1674  767.19
71       5.679  23.1548  767.54
72       5.679  23.1642  767.89
73       5.679  23.1611  768.24
74       5.679  23.0995  768.59
75       5.679  23.0961  768.94
 0       0.000   0.0000    0.00
            mV  -In(Kg/s) mmHg
```

```
DATA FILE SERIES:ZNARA.EMF
DIFFUSION COEFFICIENT DATA OF ZINC IN ARGON.25/6/86.
FLOW OF ARGON = 62cc/min(uncor). THERMOCOUPLE Pt:13%Rh/Pt.
No. OF DATA POINTS =50. CAHN R100 ELECTROBALANCE USED.
DIMENSIONS OF RE-ENTRANT CAPILLARY CHANNEL:
LENGTH L2     = 2.1008 +/- 0.0053cm.
RADIUS R2     = 0.0560 +/- 0.0010cm.
b CORRECTION = 1.000        INTERNAL PRESSURE 5.30mmHg.

RUN     EMF     -InW    PRESSURE
 1       5.226  24.3993 772.400
 2       5.226  24.5861 772.400
 3       4.802  25.5359 772.400
 4       4.802  25.5877 772.500
 5       5.786  23.4797 772.500
 6       5.786  23.5623 772.500
 7       5.786  23.3523 772.500
 8       5.786  23.3479 772.500
 9       6.124  22.6839 772.560
10       6.124  22.6461 772.630
11       6.124  22.6617 772.690
12       6.124  22.6425 772.750
13       6.569  22.0092 772.400
14       6.569  22.0054 772.170
15       5.617  23.4406 771.880
16       5.617  23.5193 771.590
17       5.617  23.5438 771.300
18       6.959  21.5322 771.260
19       6.956  21.4537 771.230
20       6.956  21.4508 771.190
21       7.465  20.7815 771.150
22       7.463  20.8186 771.150
23       7.461  20.8113 771.150
24       7.463  20.8058 771.150
25       7.849  20.3190 771.050
26       7.854  20.2940 771.050
27       7.854  20.2963 771.050
28       7.854  20.3009 771.050
29       7.854  20.2652 771.050
30       7.854  20.3324 771.050
31       8.251  19.7662 771.150
32       8.251  19.8317 771.150
33       8.251  19.7919 771.150
34       8.251  19.8045 771.150
35       8.251  19.8194 771.150
36       8.527  19.4228 770.850
37       8.527  19.4250 770.850
38       8.527  19.4467 770.850
39       8.527  19.4206 770.850
40       8.527  19.4402 770.850
41       8.793  19.0854 770.850
42       8.793  19.0477 770.850
43       8.793  19.0870 770.850
44       8.793  19.0477 770.850
45       8.793  19.0946 770.850
46       5.470  23.4497 770.850
47       5.470  23.7307 770.850
48       5.470  23.7825 770.850
49       5.470  23.8338 770.850
50       5.020  24.6053 770.850
0        0.000   0.0000   0.000
         mV     -In(Kg/s) mmHg
```

```
DATA FILE SERIES:HgHeA.EMF
DIFFUSION COEFFICIENT DATA OF MERCURY IN HELIUM. 11/3/87.
FLOW OF HELIUM      = 105cc/min. TC TYPE K  NiCr:NiAl.
No. OF DATA POINTS = 53. CAHN R100 ELECTROBALANCE USED.
DIMENSIONS OF RE-ENTRANT CAPILLARY CHANNEL:
LENGTH L2              = 1.9788E-2 m
RADIUS R2              = 0.0574E-2 m
beta correction        = 1.000   Internal Pressure = 5.00mmHg.

RUN     EMF     TEMP K  -InW    PRESSURE
 1       0.000  419.15  23.1442 778.90
 2       0.000  419.15  23.1270 778.90
 3       0.000  419.15  23.0916 778.90
 4       0.000  419.15  23.1918 778.90
 5       7.175  449.15  21.9668 778.90
 6       7.175  449.15  21.9599 778.90
 7       7.175  449.15  21.9564 778.90
 8       7.175  449.15  21.9668 778.90
 9       7.175  449.15  21.9668 778.90
10       7.175  449.15  21.9634 778.90
11       7.175  449.15  21.9564 778.90
12       7.175  449.15  21.9634 778.90
13       7.175  449.15  21.9668 778.90
14       7.175  449.15  21.9494 778.90
15       9.625  509.15  19.8909 778.65
16       9.625  509.15  19.8943 778.65
17       9.625  509.15  19.9147 778.65
18       9.625  509.15  19.9281 778.65
19       9.625  509.15  19.9347 778.65
20       9.625  509.15  19.9347 778.65
21       9.625  509.15  19.9446 778.65
22       9.625  509.15  19.9413 778.65
23       9.625  509.15  19.9380 778.65
24      10.799  538.15  19.0792 778.65
25      10.799  538.15  19.0792 778.65
26      10.799  538.15  19.0751 778.65
27      10.799  538.15  19.0751 778.65
28      10.799  538.15  19.0813 778.65
29      10.799  538.15  19.0834 778.65
30      10.799  538.15  19.0854 778.65
31      10.799  538.15  19.0834 778.65
32      10.799  538.15  19.0854 778.65
33       8.388  479.15  20.9254 778.65
34       8.388  479.15  20.8955 778.65
35       8.388  479.15  20.8854 778.65
36       8.388  479.15  20.8752 778.65
37       8.388  479.15  20.8854 778.65
38       8.388  479.15  20.8803 778.65
39       8.388  479.15  20.8854 778.65
40      12.094  570.15  18.2319 778.65
41      12.094  570.15  18.2198 778.65
42      12.094  570.15  18.2124 778.65
43      12.094  570.15  18.2124 778.65
44      12.094  570.15  18.2099 778.65
45      12.094  570.15  18.2124 778.65
46      12.094  570.15  18.2124 778.65
47      12.817  589.15  17.7532 776.35
48      12.817  589.15  17.7414 776.35
49      12.817  589.15  17.7315 776.35
50      12.817  589.15  17.7375 776.35
51      12.817  589.15  17.7454 776.35
52      12.817  589.15  17.7473 776.35
53      12.817  589.15  17.7434 776.35
 0       0.000    0.00   0.0000   0.00
            mV       C -In(Kg/s) mmHg
```

```
DATA FILE SERIES:HgH2B.EMF
DIFFUSION COEFFICIENT DATA OF MERCURY IN HYDROGEN. 5/3/87.
FLOW OF HYDROGEN   = 90cc/min. TC TYPE K  NiCr:NiAl.
No. OF DATA POINTS = 62. CAHN R100 ELECTROBALANCE USED.
DIMENSIONS OF RE-ENTRANT CAPILLARY CHANNEL:
LENGTH L2          = 1.9788E-2 m
RADIUS R2          = 0.0574E-2 m
beta correction    = 1.000   Internal Pressure = 2.36mmHg.

RUN     EMF    TEMP K  -InW    PRESSURE
 1      7.238  450.15  21.6895  771.41
 2      7.238  450.15  21.6803  771.41   ~35mg of Hg stripped
 3      7.238  450.15  21.6895  771.41    off to remove oxide
 4      7.238  450.15  21.6918  771.41    layer (270C) before
 5      7.238  450.15  21.6849  771.41    run 1
 6      7.238  450.15  21.6826  771.46
 7      8.441  480.15  20.6355  771.50    Initial weight of
 8      8.441  480.15  20.6442  771.55    Hg = 5.1317g.
 9      8.441  480.15  20.6528  771.59
10      8.441  480.15  20.6485  771.64
11      6.049  421.15  22.9138  771.68
12      6.049  421.15  22.9030  771.73
13      6.049  421.15  22.8797  771.77
14      6.049  421.15  22.8643  771.82
15      9.680  510.15  19.6415  771.86
16      9.680  510.15  19.6474  771.80
17      9.669  510.15  19.6591  771.74
18      9.669  510.15  19.6648  771.68
19      9.669  510.15  19.6706  771.63
20      9.669  510.15  19.6706  771.57
21      9.669  510.15  19.6648  771.51
22     10.851  539.15  18.9489  771.45
23     10.851  539.15  18.8654  771.39
24     10.851  539.15  18.9006  771.33
25     10.851  539.15  18.9031  771.27
26     10.851  539.15  18.9080  771.21
27     10.851  539.15  18.8781  771.16
28     10.851  539.15  18.8576  771.10
29     12.044  569.15  18.0172  771.04
30     12.044  569.15  18.0554  770.98
31     12.044  569.15  18.0467  770.92
32     12.044  569.15  18.0380  770.86
33     12.044  569.15  18.0350  770.80
34     12.044  569.15  18.0291  770.74
35     12.044  569.15  18.0321  770.69
36     12.044  569.15  18.0232  770.63
37     12.044  569.15  18.0202  770.57
38     12.044  569.15  18.0202  770.51
39     12.833  589.15  17.5119  770.45
40     12.833  589.15  17.4918  770.39

41     12.833  589.15  17.5044  770.33
42     12.833  589.15  17.4994  770.27
43     12.833  589.15  17.4969  770.22
44     12.833  589.15  17.4969  770.16
45     12.833  589.15  17.4918  770.10
46     12.833  589.15  17.4934  770.04
47     12.833  589.15  17.4934  769.98
48     12.833  589.15  17.4918  769.92
49      8.007  469.15  21.0009  769.86
50      8.007  469.15  20.9918  769.80
51      8.007  469.15  20.9825  769.75
52      8.007  469.15  20.9979  769.69
53      6.409  429.15  22.5050  769.63
54      6.409  429.15  22.5190  769.57
55      6.409  429.15  22.5249  769.51
56      6.409  429.15  22.5190  769.51
57      6.409  429.15  22.5009  769.51
58      6.409  429.15  22.5090  769.51
59      6.409  429.15  22.4969  769.51
60      6.409  429.15  22.5542  769.51
61      6.409  429.15  22.5050  769.51
62      6.409  429.15  22.5230  769.51
 0      0.000    0.00   0.0000    0.00
        mV     K       In(Kg/s) mmHg
```

```
DATA FILE SERIES:HgN2A.EMF
DIFFUSION COEFFICIENT DATA OF MERCURY IN NITROGEN. 13/3/87.
FLOW OF NITROGEN    = 90cc/min. TC TYPE K  NiCr:NiAl.
No. OF DATA POINTS = 52. CAHN R100 ELECTROBALANCE USED.
DIMENSIONS OF RE-ENTRANT CAPILLARY CHANNEL:
LENGTH L2           = 1.9788E-2 m
RADIUS R2           = 0.0574E-2 m
beta correction     = 1.000   Internal Pressure = 4.40mmHg.

RUN      EMF    TEMP K  -InW     PRESSURE
 1      6.372  429.15  24.0023  768.45
 2      6.372  429.15  24.0057  768.45    40mg of Mercury stripped
 3      6.372  429.15  23.9852  768.45    off with hydrogen before
 4      6.372  429.15  23.9955  768.45    run 1 to remove any oxid
 5      6.372  429.15  23.9357  768.45    build up.
 6      6.372  429.15  24.1022  768.45
 7      9.621  509.15  21.1426  767.50
 8      9.621  509.15  21.1367  767.50
 9      9.621  509.15  21.1126  767.50
10      9.621  509.15  21.1602  767.50
11      9.621  509.15  21.1485  767.50
12      9.621  509.15  21.1485  767.50
13     10.857  540.15  20.2894  767.50
14     10.857  540.15  20.2322  767.50
15     10.857  540.15  20.2636  767.50
16     10.857  540.15  20.2752  767.50
17     10.857  540.15  20.2612  767.50
18     10.857  540.15  20.2752  767.50
19     10.857  540.15  20.2564  767.50
20      8.402  479.15  22.2173  764.40
21      8.402  479.15  22.1078  764.40
22      8.402  479.15  22.0972  764.40
23      8.402  479.15  22.0835  764.40
24      8.402  479.15  22.0995  764.40
25      7.212  450.15  23.1880  759.00
26      7.212  450.15  23.1399  759.00
27      7.212  450.15  23.1569  759.00
28      7.212  450.15  23.1117  759.00
29      7.212  450.15  23.1632  759.00
30      7.212  450.15  23.1420  759.00
31      7.212  450.15  23.1356  759.00
32      7.212  450.15  23.1160  759.00
33      0.000  519.15  20.7891  745.25
34      0.000  519.15  20.8113  745.25
35      0.000  519.15  20.8222  745.25
36      0.000  519.15  20.8330  745.25
37      0.000  519.15  20.8330  745.25
38      0.000  519.15  20.8168  745.25
39      0.000  519.15  20.8222  745.25
40      0.000  519.15  20.8276  745.25

41      0.000  519.15  20.8330  745.25
42      0.000  519.15  20.8490  745.25
43     12.086  570.15  19.3937  758.25
44     12.086  570.15  19.4095  758.25
45     12.086  570.15  19.4139  758.25
46     12.086  570.15  19.4195  758.25
47     12.086  570.15  19.4162  758.25
48     12.086  570.15  19.4305  758.25
49     12.873  590.15  18.8440  758.25
50     12.873  590.15  18.8440  758.25
51     12.873  590.15  18.8440  758.25
52     12.873  590.15  18.8321  758.25
53     12.873  590.15  18.8440  758.25
 0      0.000    0.00   0.0000    0.00
          mV      K    -In(Kg/s) mmHg
```

```
DATA FILE SERIES:HgArA.EMF
DIFFUSION COEFFICIENT DATA OF MERCURY IN ARGON. 8/3/87.
FLOW OF ARGON        = 90cc/min. TC TYPE K  NiCr:NiAl.
No. OF DATA POINTS = 50. CAHN R100 ELECTROBALANCE USED.
DIMENSIONS OF RE-ENTRANT CAPILLARY CHANNEL:
LENGTH L2            = 1.9788E-2 m
RADIUS R2            = 0.0574E-2 m
beta correction      = 1.000   Internal Pressure = 5.19mmHg.

RUN     EMF     TEMP K  -InW    PRESSURE
 1        0.000 429.15  24.1940 773.04
 2        0.000 429.15  24.2306 773.04
 3        7.181 449.15  23.4550 773.04
 4        7.181 449.15  23.4353 773.04
 5        7.181 449.15  23.4393 773.04
 6        7.181 449.15  23.3863 773.04
 7        9.589 508.15  21.3942 773.08
 8        9.589 508.15  21.4377 773.12
 9        9.589 508.15  21.4199 773.17
10        9.589 508.15  21.4109 773.21
11        9.589 508.15  21.4199 773.25
12        9.589 508.15  21.4244 773.29
13        9.589 508.15  21.4154 773.33
14        9.589 508.15  21.4109 773.37
15        9.589 508.15  21.4244 773.42
16        9.589 508.15  21.4199 773.46
17       10.793 538.15  20.5489 773.49
18       10.793 538.15  20.5678 773.54
19       10.793 538.15  20.5771 773.58
20       10.793 538.15  20.5771 773.62
21       10.793 538.15  20.5631 773.67
22       10.793 538.15  20.5724 773.71
23       10.793 538.15  20.5584 773.75
24       10.793 538.15  20.5584 773.79
25       12.046 569.15  19.7099 773.77
26       12.046 569.15  19.7072 773.75
27       12.046 569.15  19.7016 773.73
28       12.046 569.15  19.7127 773.71
29       12.046 569.15  19.7209 773.73
30       10.267 525.15  20.9400 773.73
31       10.267 525.15  20.9056 773.68
32       10.267 525.15  20.8854 773.67
33       10.267 525.15  20.9303 773.64
34       10.267 525.15  20.9303 773.62
35       10.267 525.15  20.9155 773.60
36       10.267 525.15  20.9106 773.54
37       12.905 590.15  19.1373 773.54
38       12.905 590.15  19.0974 773.54
39       12.905 590.15  19.1263 773.54
40       12.905 590.15  19.1385 773.54
41       12.905 590.15  19.1101 773.54
42       12.905 590.15  19.1138 773.54
43       12.905 590.15  19.1113 773.54
44       12.905 590.15  19.1126 773.54
45       12.905 590.15  19.1101 773.54
46       12.905 590.15  19.1324 773.54
47       12.905 590.15  19.1263 773.54
48        8.412 479.15  22.3584 773.54
49        8.412 479.15  22.3135 773.54
50        8.412 479.15  22.3460 773.54
 0        0.000   0.00   0.0000   0.00
          mV      K     In(Kg/s) mmHg
```

DATA FILE SERIES:ZNCL2AR.EMF ZNCL2ARA.EMF
EQUILIBRIUM OF ZnCl2 IN ARGON. DATE 25/11/85.
UNCORRECTED FLOW RATE Ar=70 cc/min. TC Pt:Pt/13%Rh.
No. OF DATA POINTS=95. FOR ZnCl2. CAHN R100 USED.
DIMENSIONS OF REAR ENTRY CAPILLARY CHANNEL:
LENGTH L=2.1778+/-0.0111cm. RADIUS 0.0598+/-0.0017cm.
CROSS-SECTIONAL AREA=4.5005E-6+/-9.4E-10.

RUN	EMF	TEMP C	-InW	PRESSURE	
4	4.120	467.553	24.1195	765.420	
5	4.117	467.273	24.1607	764.790	CHARGED ZnCL2 IN BOTTLE
6	4.117	467.273	24.2019	765.370	(DRY BOX 15->110 ppm(v)H20
7	4.117	467.273	24.1700	765.940	LOADED BOTTLE INTO MEM RI
8	4.334	487.417	23.6127	765.940	EVACUATED FOR 48HRS RAISI
9	4.334	487.417	23.5911	766.250	25-335C,PRESSURE 0.15-0.8
10	4.334	487.417	23.5741	766.560	NEGLIGIBLE WT LOSS BELOW
11	4.334	487.417	23.6306	766.880	FLUSHED WITH HCL FOR 18HR
12	4.563	508.479	23.1893	767.190	TEMP 335-408C. ABORTED RU
13	4.563	508.479	23.1674	767.430	1-3 NOT SETTLED DOWN.
14	4.563	508.479	23.1243	767.670	
15	4.563	508.479	23.1485	767.920	
16	4.563	508.479	23.1084	768.160	
17	4.563	508.479	23.0904	768.640	
18	4.563	508.479	23.1646	768.400	
19	4.778	528.078	22.5610	768.770	
20	4.778	528.078	22.5892	768.890	
21	4.778	528.078	22.6036	769.020	
22	4.778	528.078	22.6030	769.140	
23	4.778	528.078	22.6030	769.270	
24	4.778	528.078	22.6112	769.390	
25	4.992	547.425	22.1640	769.340	
26	4.993	547.515	22.1414	768.790	
27	5.000	548.146	22.1553	768.790	
28	5.000	548.146	22.0636	767.090	
29	4.993	547.515	22.1220	767.090	
30	4.996	547.785	22.1240	767.090	
31	5.209	566.884	21.6226	766.590	
32	5.209	566.884	21.6500	766.590	
33	5.209	566.884	21.6803	766.340	
34	5.209	566.884	21.6945	766.090	
35	5.209	566.884	21.6940	765.840	
36	5.434	586.897	21.2550	765.830	
37	5.434	586.897	21.2313	765.830	
38	5.434	586.897	21.2353	765.820	
39	5.434	586.897	21.2313	765.810	
40	5.434	586.897	21.2248	765.800	
41	5.434	586.897	21.2277	765.800	
42	5.434	586.897	21.2131	765.790	
43	5.657	606.578	20.7892	765.790	
44	5.657	606.578	20.8259	765.750	
45	5.657	606.578	20.8091	765.710	
46	5.657	606.578	20.8047	765.670	
47	5.657	606.578	20.8089	765.630	
48	5.657	606.578	20.8030	765.590	
49	5.884	626.467	20.3583	765.640	
50	5.884	626.467	20.3822	765.690	
51	5.884	626.467	20.3931	765.740	
52	5.884	626.467	20.3866	765.790	
53	5.884	626.467	20.3780	765.840	
54	6.120	646.941	19.9504	765.840	
55	6.120	646.941	19.9511	765.790	
56	6.120	646.941	19.9511	765.740	
57	6.120	646.941	19.9575	765.690	
58	6.120	646.941	19.9575	765.640	
59	6.120	646.941	19.9661	765.590	
60	6.349	666.640	19.5193	765.540	
61	6.349	666.640	19.5469	765.540	
62	6.349	666.640	19.5430	765.540	
63	6.349	666.640	19.5391	765.540	
64	6.349	666.640	19.5237	765.540	
65	6.349	666.640	19.5469	765.540	
66	6.349	666.640	19.5391	765.540	
67	6.573	685.751	19.1022	765.540	
68	6.573	685.751	19.0887	765.530	
69	6.573	685.751	19.0946	765.510	
70	6.573	685.751	19.0887	765.500	
71	6.573	685.751	19.0931	765.480	
72	6.573	685.751	19.1113	765.470	
73	6.573	685.751	19.1218	765.450	
74	6.573	685.751	19.1022	765.440	
75	6.806	705.471	18.5691	765.430	
76	6.806	705.471	18.5656	765.410	
77	6.806	705.471	18.5517	765.400	
78	6.806	705.471	18.5535	765.380	
79	6.806	705.471	18.5630	765.370	
80	6.806	705.471	18.5622	765.350	
81	6.806	705.471	18.5656	765.340	
82	4.272	481.680	23.8652	766.840	
83	4.272	481.680	23.8693	768.340	
84	4.272	481.680	23.8936	769.840	RUN 84 NEW ARGON CYLINDE
85	3.932	449.950	24.8404	766.520	INTRODUCED INTO MEM RIG.
86	3.923	449.104	24.9109	765.130	
87	3.914	448.257	24.8451	759.620	
88	3.580	416.587	25.8789	761.230	RUN 88 DOOR LEFT OPENED
89	3.575	416.109	25.8733	764.190	TEMP DROP BY 10C. 2nd HA
90	3.575	416.109	25.9341	765.540	OF RESULT ABORTED(PLATEA
91	3.386	397.956	26.4157	765.540	NOTE RUN 88= RUN 89.THER
92	3.376	396.991	26.3931	768.740	RUN 88 HAS NOT FORMED AN
93	3.198	379.722	27.1101	774.700	OXIDE LAYER.

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 94        3.203  380.209 27.6716  776.820
 95        3.205  380.404 27.0768  778.940
 96        3.208  380.697 27.6236  780.790
 97        3.212  381.086 27.5636  776.590
 98        3.212  381.086 27.2719  778.320
  0       0.000     0.000  0.0000    0.000
          mV       C       In(Kg/s) mmHg
 DATA FILE SERIES:ZNCL2AR.EMF                          ZNCL2ARB.EMF
 ZnCl2 doped with 0.3% of H20 by wt in Ar. 6/2/86.
UNCORRECTED FLOW RATE Ar=70 cc/min. TC Pt:Pt/13%Rh.
 No. OF DATA RUNS=32. CAHN BALANCE R100 USED.
 DIMENSION OF REAR ENTRY CAPILLARY CHANNEL:
 LENGTH L=2.1778+/-0.0111cm. RADIUS 0.0598+/-0.0017cm
 CROSS-SECTIONAL AREA=4.5005E-6+/-9.4E-10m2.


 RUN      EMF     TEMP C  -InW    PRESSURE
  1        3.384  397.762 26.0383  777.440
  2        3.384  397.762 26.2669  777.440  USING WATER ENTRAINMENT
  3        3.384  397.762 26.1874  777.440  METHOD 0.15% BY WT INCREA
  5        3.670  425.170 25.2508  777.970  0.15% BY WT. ALSO PICKED
  6        3.670  425.170 25.2690  778.510  BY EXPOSING SAMPLE TO ATM
  7        3.670  425.170 25.2764  779.040  RUN 4 AND 8 ROGUE VALUES.
  9        4.018  458.020 24.2095  776.090
 10        4.018  458.020 24.1982  773.140  N.B.
 11        4.499  502.612 22.9740  773.140  ZNCL2 FROM EXPT ZNCL2ARA.
 12        4.499  502.612 22.9743  772.130  AFTER THIS EXPT ON CHANNE
 13        4.499  502.612 22.9702  771.130  FULL OF 'PIT HOLES' ON IT
 14        4.499  502.612 23.0911  770.120  OUTSIDE. INNER DIMENSION
 15        4.499  502.612 23.0383  769.110  SEEM O.K. ZNCL2 AND ZNO M
 16        4.499  502.612 23.0233  768.100  DECOMPOSES SILICA(VERY SL
 17        4.499  502.612 23.0070  767.100  FURNACE STRIPPED AND REBU
 18        4.499  502.612 23.0333  766.090  MAY ALTER PROFILE BY 2C W
 19        4.928  541.655 22.0629  766.090  COMPARING DATA WITH EXPT
 20        4.928  541.655 22.0203  765.790  ZNCL2ARA.EMF.
 21        4.928  541.655 22.0530  765.490
 22        4.928  541.655 22.0478  765.190
 23        4.928  541.655 22.0323  764.890  COMPARING THIS DOPED EXPT
 24        4.928  541.655 22.0444  764.590  PREVIOUS ONE. PLOTTING -I
 25        5.484  591.323 20.9360  764.290  1/TEMPK INDICATES NO DIFF
 26        5.484  591.323 20.9155  763.990
 27        5.484  591.323 20.9303  763.690
 28        5.484  591.323 20.9339  763.390  RUN ROGUE VALUES:
 29        5.484  591.323 20.9217  763.090   4  3.670  25.1214  777.4
 30        5.484  591.323 20.9356  763.090   8  4.018  24.3040  779.0
 31        5.484  591.323 20.9056  763.090
 32        3.078  367.985 27.4265  760.790
 33        3.078  367.985 27.1721  760.790
 34        3.079  368.083 27.4158  760.790
  0       0.000     0.000  0.0000    0.000
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          mV       C       In(Kg/s) mmHg
 DATA FILE SERIES:ZNCL2AR.EMF                          ZNCL2ARC.EMF
 EQUILIBRIUM OF ZnCl2(ii) IN ARGON. DATE 29/2/86.
 UNCORRECTED FLOW RATE Ar=80 cc/min. TC Pt:13%Rh/Pt.
No. OF DATA POINTS = 65. CAHN MICROBALANCE USED R100.
 INTERNAL PRESSURE OF MEM = 6.73 mmHg.
 DIMENSIONS OF REAR ENTRY CAPILLARY CHANNEL:
 LENGTH L=2.0043 +/-0.0054cm. RADIUS R=0.0565+/-0.0018cm.


 RUN      EMF     TEMP C  -InW    PRESSURE
  1        5.028  550.664 22.1135  756.980
  2        5.030  550.844 22.1016  756.980   Wt. of sample 514.92mg.
  3        5.030  550.844 22.1286  756.870  Charged ZnCl2 in bottle-
  4        5.030  550.844 22.1264  756.760  dry box 5->8 ppm(v)H20,2h
  5        5.028  550.664 22.0995  756.640   Loaded it into MEM rig
  6        5.669  607.633 20.8833  756.530  evacuated for 91hrs, rais
  7        5.669  607.633 20.8981  756.580  temperature from 25-> 270
  8        5.669  607.633 20.8879  756.630  pressure 0.0015-> 0.005 m
  9        5.669  607.633 20.8777  756.680   Flushed with HCl for 47h
 10        5.669  607.633 20.8700  756.730  temperature 270-> 531 C.
 11        5.669  607.633 20.8955  756.780
 12        6.347  666.468 19.6643  756.830
 13        6.335  665.439 19.6573  756.630    N.B. Flow rate of argon
 14        6.336  665.525 19.6882  756.430   increased from 70 cc/min
 15        6.335  665.439 19.6932  756.030   to flush vapour well fro
 16        6.332  665.183 19.6848  756.030   tip of channel and hopef
 17        4.653  516.704 22.9814  755.830   eliminate minor weight l
 18        4.653  516.704 23.0048  755.930   due to decomposition in
 19        4.653  516.704 22.9978  756.810   region.
 20        4.653  516.704 22.9370  757.690
 21        4.201  475.092 24.0583  758.570
 22        4.201  475.092 24.0698  759.450
 24        4.201  475.092 24.1697  760.330   Run 23 rogue value:
 25        4.192  474.256 24.0466  764.430   4.201  24.2997  760.33.
 26        3.552  413.909 26.0627  767.830
 28        3.552  413.909 26.0067  774.430   Run 27 rogue value:
 29        3.081  368.279 27.6563  770.830   3.552  25.6817  770.83.
 30        3.081  368.279 27.6756  767.230
 31        3.954  452.018 24.8410  770.110
 32        3.954  452.018 24.8642  770.080
 33        3.954  452.018 24.7951  771.030
 34        5.932  630.646 20.4372  771.230
 35        5.929  630.385 20.4436  771.250
 36        5.930  630.472 20.4515  771.270
 37        5.929  630.385 20.4356  771.290
 38        5.928  630.298 20.4541  771.310
 39        6.090  644.349 20.1550  771.320
 40        6.086  644.003 20.1585  771.370
 41        6.089  644.263 20.1594  771.410   Run 42
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43        6.087  644.090 20.1611  771.490   6.088  20.1291  771.45
44        6.254  658.487 19.8543  771.530
45        6.253  658.401 19.8515  771.530
46        6.253  658.401 19.8486  771.530
47        6.253  658.401 19.8442  771.530
48        6.252  658.315 19.8723  771.530
49        6.420  672.714 19.5339  771.570
50        6.419  672.628 19.5456  771.610
51        6.418  672.543 19.5674  771.660
52        6.417  672.457 19.5547  771.700
53        6.418  672.543 19.5585  771.740
54        6.576  686.006 19.2369  771.780
55        6.581  686.431 19.2236  771.280
56        6.579  686.261 19.2435  771.290
57        6.577  686.091 19.2316  771.290   Run 59 eq. not reached
58        6.577  686.091 19.2316  771.300   6.728    18.9545 771.30
60        6.694  696.012 19.0168  771.310
61        6.689  695.589 19.0283  771.310
62        6.691  695.758 19.0035  771.320
63        6.689  695.589 18.9917  771.320
64        6.692  695.843 18.9780  771.330
65        5.830  621.757 20.6162  771.330
66        5.830  621.757 20.6045  771.330
67        5.831  621.844 20.6146  771.330   Run 68
69        3.051  365.332 27.5710  770.830   5.831  20.7169  771.33
70        3.051  365.332 27.4351  768.830
 0      0.000      0.000 0.0000     0.000
        mV       C       In(Kg/s) mmHg
DATA FILE SERIES:ZNCL2AR.EMF                       ZNCL2ARD.EMF
EQUILIBRIUM OF DAMPED ZnCl2(ii) IN ARGON. 17/3/86.
UNCORRECTED FLOW RATE Ar=80cc/min. TC Pt:13%Rh/Pt.
No. OF DATA POINTS = 51. CAHN MICROBALANCE USED R100.
INTERNAL PRESSURE OF MEM = 6.73 mmHg.
DIMENSIONS OF REAR ENTRY CAPILLARY CHANNEL:
LENGTH L=2.0043 +/-0.0054cm. RADIUS R=0.0565+/-0.0018cm.


RUN      EMF      TEMP C  -InW     PRESSURE
 1        3.557  414.388 25.8041  765.580
 2        3.551  413.814 26.0014  770.130  Expt. carried on from
 3        4.192  474.256 24.1410  708.030 ZnCl2(ii) dated 29/2/86
 4        4.192  474.256 24.1961  766.980 (ZNCL2ARC.EMF).
 5        4.192  474.256 24.3068  765.930
 6        5.070  554.438 22.0995  766.870  Injected water vapour und
 7        5.070  554.438 22.0880  767.810 vacuum (0.2mmHg) in MEM ri
 8        5.070  554.438 22.1286  768.750 Wt increased by 2.5%
 9        5.070  554.438 22.1240  769.690 (334.17mg --> 342.51mg).
10        5.070  554.438 22.1286  770.630
11        4.635  515.062 23.0894  771.570  Heated sample upto 110 C
12        4.635  515.062 23.1095  772.510  held for 17hrs. Wt loss 4
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13        4.635  515.062 23.1177  773.450  (342.51mg --> 338.425mg).
14        4.635  515.062 23.1111  774.390
15        5.712  611.409 20.8700  782.060   Final wt increased after
16        5.712  611.409 20.8473  775.370  heating 1.27%.
17        5.712  611.409 20.8879  775.410
18        5.712  611.409 20.8803  775.440
19        5.928  630.298 20.4462  775.480
20        5.928  630.298 20.4774  775.470
21        5.928  630.298 20.4748  775.470
22        5.928  630.298 20.4541  775.460
23        5.928  630.298 20.4697  775.450   Runs 24-30
31        6.265  659.433 19.8486  775.390  aborted temp not read.
32        6.265  659.433 19.8500  775.380
33        6.265  659.433 19.8615  775.380
34        6.265  659.433 19.8442  775.370
36        6.379  669.208 19.6397  775.350   Run 35 rogue value
37        6.379  669.208 19.6326  775.350  6.382 19.6631 775.35
38        6.379  669.208 19.6374  775.340
39        6.600  688.044 19.2128  775.330
40        6.599  687.959 19.2238  775.340
41        6.596  687.704 19.2263  775.340
42        6.596  687.704 19.2303  775.350
43        6.708  697.196 19.0018  775.350
44        6.709  697.280 18.9414  775.360
45        6.707  697.111 18.9797  775.360
46        6.709  697.280 18.9883  775.370
47        6.101  645.300 20.1523  775.370
48        6.106  645.732 20.1108  775.380
49        6.106  645.732 20.1291  775.380
50        6.107  645.818 20.1181  770.410  Runs 51-53 are unexpectly
51        3.066  366.807 28.3430  765.450 Will do some further runs
52        3.071  367.297 27.9865  756.230 higher temp.
53        3.076  367.788 28.6232  747.280   N.B. low pressure correc
54        3.306  390.219 26.3331  744.110
55        3.299  389.541 26.7972  750.130
56        3.294  389.055 26.9731  753.830
57        3.294  389.055 27.0379  757.530
58        3.292  388.862 27.0925  756.880
 0      0.000      0.000 0.0000     0.000
        mV       C       In(Kg/s) mmHg
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DATA FILE SERIES:ZNSH2.EMF                              ZNSH2A.EMF
EQUILIBRIUM OF ZnS IN H2.ALDICH GOLD LABEL ELEC.GRADE.
DATE 16/6/85. FLOW RATE H2=90cc/min. TC Pt:Pt/13%Rh.
No. OF DATA POINTS=29 FOR ZINC BLENDE. CAHN R100 USED.
DIMENSIONS OF CAPILLARY CHANNEL:
LENGTHS L1=0.0663+/-0.0052cm L2=1.7936+/-0.0077cm.
RADII   R1=0.0774+/-0.0045cm R2=0.0559+/-0.0028cm.
b CORRECTION [1+(R2.L1/R1.L2)]=1.0267.

RUN     EMF     TEMP C  -InW    PRESSURE
 3      10.032  964.144 22.4167  765.910
 4      10.033  964.221 22.3552  766.010 RUN 1 AND 2 TEMP RAISED
 5       9.613  931.888 22.7570  765.960 TO 650C WT LOSS OF 'H20'
 6       9.614  931.966 22.7763  765.935 3.5% BY WT OF SAMPLE
 7       9.327  909.662 23.0203  765.960
 8       9.329  909.818 23.0238  766.260
 9       9.054  888.284 23.2324  766.510
10       9.054  888.284 23.3666  766.510
11       9.053  888.205 23.2814  766.610
12       7.383  753.638 25.6066  766.185
13       7.383  753.638 27.9389  765.485
14       7.383  753.638 25.8430  764.635
15       7.141  733.549 24.8989  764.035
16       7.139  733.383 25.5511  763.560
17       7.140  733.466 26.3183  762.860
18       7.140  733.466 25.8009  762.485
19       7.140  733.466 26.9518  762.135
20       7.137  733.216 25.6518  761.635
21       6.887  712.289 26.2497  760.010
22       6.885  712.121 27.4368  758.510
23       9.321  909.194 23.1356  759.910
24       9.319  909.038 23.0220  758.860
25       7.647  775.373 25.0582  760.185
26       8.749  864.204 23.9408  761.285
27       8.748  864.125 23.8249  761.410
28       8.746  863.967 23.7545  761.460
29       8.075  810.228 24.4152  761.260  RUN 32 AND 33 IN ARGON.
30       8.077  810.389 24.3012  761.235  THERMOMOLECULAR WT
31       7.383  753.638 24.6954  759.000  0.05mg.THEN AFTER WDOT 0
 0      0.000     0.000  0.0000    0.000
        mV      C       In(Kg/s) mmHg
DATA FILE SERIES:ZNSH2.EMF                             ZNSH2B.EMF
EQUILIBRIUM OF ZNS IN H2.BAKED FOR 36HRS MIN.>1050C IN Ar.
DATE 7/8/85.FLOW RATE H2=90cc/min. TC Pt:Pt/13%Rh.
No. OF DATA POINTS=58 for WURTZITE. CAHN R100 USED.
DIMENSIONS OF CAPILLARY CHANNEL:
LENGTHS L1=0.0471+/-0.0105cm L2=2.0809+/-0.0090cm.
RADII  2R1=0.2577+/-0.02705cm 2R2=0.08573+/-0.0030cm.
b CORRECTION [1+(R2.L1/R1.L2)]=1.0075.
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RUN     EMF     TEMP C  -InW     PRESSURE
 1      11.275 1057.840 21.8147  758.370
 2      11.275 1057.840 21.8625  758.145
 3      11.276 1057.914 21.8638  758.045
 4      11.275 1057.840 21.8755  757.845
 5      11.415 1068.217 21.7747  757.970
 6      11.415 1068.217 21.7630  758.295
 7      11.711 1090.047 21.5342  758.495
 8      11.712 1090.120 21.5439  758.620
 9      11.713 1090.193 21.5424  758.720
10      11.713 1090.193 21.5251  758.970
11      12.002 1111.364 21.3253  758.920
12      12.002 1111.364 21.3253  758.920
13      12.003 1111.438 21.3222  758.920  MEM RIG SHUT DOWN.
14      12.007 1111.729 21.5689  758.695  RUNS 14-16 BETA-->ALPHA
15      12.008 1111.803 21.4362  758.520  ZnS  TRANSITION.
16      12.010 1111.949 21.3425  758.495  14-15 OUTLIERS.
17      12.012 1112.095 21.3033  758.370
18      12.012 1112.095 21.3150  758.160
19      12.012 1112.095 21.3077  757.935
20      12.014 1112.241 21.2837  757.795
21      12.015 1112.313 21.3148  757.780
22      12.015 1112.313 21.3111  757.800
23      12.015 1112.313 21.3179  757.825
24      12.015 1112.313 21.3194  757.355
25      12.015 1112.313 21.3311  756.870
26      12.311 1133.851 21.1198  756.845
27      12.313 1133.995 21.1184  756.820
28      12.312 1133.923 21.1153  756.820
29      12.313 1133.995 21.1118  756.820
30      12.614 1155.752 20.9169  756.820
31      12.614 1155.752 20.9134  756.820
32      12.614 1155.752 20.9062  756.820
33      12.614 1155.752 20.9037  756.820
34      12.614 1155.752 20.9032  756.570
35      12.480 1146.084 21.0054  756.245
36      12.480 1146.084 21.0066  756.120
37      12.480 1146.084 20.9982  756.020
38      12.481 1146.156 20.9901  755.920
39      12.481 1146.156 20.9865  755.820
40      12.482 1146.229 20.9964  755.820
41      11.166 1049.736 21.9628  755.820
42      11.166 1049.736 21.9708  755.820
43      11.166 1049.736 21.9738  755.820
44      11.296 1059.398 21.8760  755.820
45      11.297 1059.473 21.8616  755.820
46      11.296 1059.398 21.8732  755.820
47      11.452 1070.954 21.7508  755.760
48      11.452 1070.954 21.7359  755.835
49      11.452 1070.954 21.7639  755.800
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50      11.452 1070.954 21.7585  755.675
51      11.602 1082.025 21.6247  755.570
52      11.602 1082.025 21.6065  755.570
53      11.732 1091.590 21.5342  755.570
54      11.732 1091.590 21.5426  755.720
55      12.193 1125.281 21.2111  755.845
56      12.193 1125.281 21.2143  755.920
57      12.188 1124.918 21.2049  755.980
58      12.193 1125.281 21.1843  756.020
 0      0.000     0.000  0.0000    0.000
        mV       C       In(Kg/s) mmHg
DATA FILE SERIES:ZNSH2.EMF                       ZNSH2C.EMF
EQUILIBRIUM OF ZnS IN H2. ALDRICH GOLD LABEL ELEC.GRADE.
DATE 15/5/86. FLOW RATE H2=90cc/min. Pt:Pt13%Rh.
No. OF DATA POINTS=55. FOR ZINC BLENDE. CAHN R100 USED.
DIMENSION OF RE-ENTRANT CAPILLARY CHANNEL:
LENGTH L2      = 2.0043 +/- 0.0054cm.
RADIUS R2      = 0.0563 +/- 0.0018cm.
b CORRECTION = 1.0000

RUN     EMF     TEMP C  -InW    PRESSURE
 1       8.662  857.297 23.6732  767.150
 2       8.662  857.297 23.6968  765.660      ESTD 'WATER' LOSS
 3       8.662  857.297 23.6853  764.180      AT 110C IN H2
 4       8.662  857.297 23.6735  762.690      =100*(0.019/0.3984)
 5       8.662  857.297 23.8800  761.200      =4.7%
 6       9.339  910.599 23.1595  759.400
 7       9.331  909.975 23.0902  758.650
 8       9.331  909.975 23.1308  757.900
 9       9.331  909.975 23.0964  757.150
10       9.331  909.975 23.0352  756.400
11      10.276  982.767 22.2139  756.630
12      10.276  982.767 22.1697  756.800
13      10.276  982.767 22.1725  756.970
14      10.276  982.767 22.1976  757.300
15      10.276  982.767 22.1976  756.750
16       9.744  942.012 22.6284  756.630
17       9.744  942.012 22.6230  756.500
18       9.744  942.012 22.6496  756.380
19       9.744  942.012 22.6583  756.250
20       9.744  942.012 22.6461  756.130
21       9.744  942.012 22.6478  756.000
22      10.482  998.398 21.9992  756.070
23      10.482  998.398 22.0017  756.140
24      10.482  998.398 21.9763  756.210
25      10.482  998.398 21.9967  756.280
26      10.482  998.398 21.9840  756.360
27      10.482  998.398 21.9789  756.430
28      10.482  998.398 21.9916  756.500
29       9.558  927.627 22.8797  757.830
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30       9.558  927.627 22.7712  759.160
31       9.558  927.627 22.7324  760.490
32       9.558  927.627 22.8151  761.810
33       9.558  927.627 22.8225  763.140
34       9.558  927.627 22.8558  764.470
35       9.558  927.627 22.8371  765.800
36       9.077  890.091 23.4029  765.790
37       9.077  890.091 23.3905  765.780
38       9.077  890.091 23.2655  765.770
39       9.077  890.091 23.3440  765.760
40       8.481  842.870 23.9957  765.750
41       8.481  842.870 23.8760  765.900
42       7.691  778.978 24.9696  765.750
43       7.691  778.978 24.9333  765.750
44       7.691  778.978 24.9626  765.750
45       7.691  778.978 25.0439  765.750
46       7.691  778.978 24.9486  765.750
47       8.061  809.095 24.6412  765.750
48       8.061  809.095 24.4021  765.750
49       8.061  809.095 24.4786  765.750
50       8.061  809.095 24.4312  765.750
51       8.061  809.095 24.5299  765.750
52       8.061  809.095 24.3388  765.750
53       8.061  809.095 24.4616  765.750
54       8.061  809.095 24.5036  765.750
55       8.061  809.095 24.4723  765.750
 0      0.000     0.000  0.0000    0.000
        mV       C       In(Kg/s) mmHg
DATA FILE SERIES:ZNSH2.EMF                       ZNSH2D.EMF
EQUILIBRIUM OF ZnS IN H2. ALDRICH GOLD LABEL ELEC. GRADE.
DATE 2/9/86. FLOW RATE H2=90cc/min. Pt:Pt/13%Rh.
No. OF DATA POINTS=     FOR WURTZITE. CAHN R100 USED.
DIMENSIONS OF RE-ENTRANT CAPILLARY CHANNEL:
LENGTH L2       = 2.1008 +/- 0.0053cm.
RADIUS R2       = 0.0560 +/- 0.0010cm.
b CORRECTION    = 1.0000

RUN     EMF     TEMP C  -InW    PRESSURE
10      10.865 1027.250 21.7579  761.500
11      10.865 1027.250 21.7600  761.500  NOT REACHED EQM.
12      10.865 1027.250 21.7472  761.500  1  10.865 21.7811 761.50
13      10.865 1027.250 21.7600  761.500  2  10.865 21.8179 761.50
14      10.865 1027.250 21.7642  761.500  3  10.865 21.7831 761.50
15      10.865 1027.250 21.7831  761.500  4  10.865 21.7727 761.50
16      10.865 1027.250 21.7642  761.500  5  10.865 21.7450 761.50
17      10.865 1027.250 21.7579  761.500  6  10.865 21.7664 761.50
18      10.865 1027.250 21.7600  761.500  7  10.865 21.7852 761.50
19      10.865 1027.250 21.7706  761.500  8  10.865 21.7811 761.50
20      10.865 1027.250 21.7385  761.500  9  10.865 21.7685 761.50
21      10.865 1027.250 21.7428  761.500
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22        10.865 1027.250 21.7254  774.250
23        11.124 1046.608 21.6037  774.250
24        11.124 1046.608 21.5208  774.250
25        11.124 1046.608 21.5422  774.250
26        11.124 1046.608 21.5734  774.250
27        11.124 1046.608 21.5683  774.250
28        11.124 1046.608 21.5474  774.250
29        11.124 1046.608 21.5912  774.250
30        11.124 1046.608 21.5734  774.250
31        11.124 1046.608 21.5887  774.250
32        11.124 1046.608 21.6136  774.250
33        11.124 1046.608 21.6356  774.250
34        11.124 1046.608 21.5785  774.250
35        11.124 1046.608 21.5474  774.250
36        11.124 1046.608 21.5501  774.250
37        11.124 1046.608 21.5527  774.250
38        11.124 1046.608 21.5631  774.250
39        11.124 1046.608 21.5605  774.250
40        11.124 1046.608 21.5342  774.250
41        11.124 1046.608 21.5631  774.250
42        11.124 1046.608 21.5657  774.250
43        11.124 1046.608 21.5683  774.250
44        11.124 1046.608 21.5657  774.250
45        11.124 1046.608 21.5657  774.250
46        11.124 1046.608 21.5734  774.250
47        11.124 1046.608 21.5683  774.250
48        11.124 1046.608 21.5708  774.250
49        11.124 1046.608 21.5708  774.250
50        11.124 1046.608 21.5887  774.250
51        11.378 1065.478 21.4084  774.250
52        11.378 1065.478 21.3672  774.250
53        11.378 1065.478 21.3620  774.250
54        11.378 1065.478 21.3714  774.250
55        11.896 1103.615 20.9933  774.250
56        11.896 1103.615 21.0099  774.250
57        11.896 1103.615 21.0219  774.250
58        11.896 1103.615 20.9933  774.250
59        11.896 1103.615 21.0009  774.250
60        12.155 1122.518 20.7891  774.250
61        12.155 1122.518 20.8002  774.250
62        12.155 1122.518 20.8002  774.250
63        12.155 1122.518 20.8094  774.250
64        12.550 1151.138 20.5309  774.250
65        12.550 1151.138 20.5471  774.250
66        12.550 1151.138 20.5291  774.250
67        12.550 1151.138 20.5291  774.250
68        12.550 1151.138 20.5254  774.250
69        12.550 1151.138 20.5381  774.250
70        12.550 1151.138 20.5309  774.250
71        12.550 1151.138 20.5435  774.250
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72        12.687 1161.008 20.4455  774.250
73        12.687 1161.008 20.4554  774.250
74        12.687 1161.008 20.4671  774.250
75        12.687 1161.008 20.4613  774.250
76        12.321 1134.575 20.7132  774.250
77        12.321 1134.575 20.6979  774.250
78        12.321 1134.575 20.6824  774.250
79        12.321 1134.575 20.6730  774.250
80        12.321 1134.575 20.6699  774.250
81        12.321 1134.575 20.6793  774.250
82        12.321 1134.575 20.6824  774.250
83        11.673 1087.253 21.1485  772.450
84        11.673 1087.253 21.1367  772.450
85        11.673 1087.253 21.1485  772.450
86        11.673 1087.253 21.1446  772.450
87        11.673 1087.253 21.1485  772.450
88        11.673 1087.253 21.1563  772.450
89        11.673 1087.253 21.1524  772.450
90        11.301 1059.770 21.4094  772.450
91        11.301 1059.770 21.4244  772.450
92        11.301 1059.770 21.4362  772.450
93        11.301 1059.770 21.4333  772.450
94        11.301 1059.770 21.4362  772.450
95        11.301 1059.770 21.4362  772.450
96        11.301 1059.770 21.4450  772.450
97        11.301 1059.770 21.4392  772.450
98        11.301 1059.770 21.4362  772.450
99        11.301 1059.770 21.4392  772.450
 0        0.000     0.000  0.0000    0.000
          mV      C       In(Kg/s) mmHg
DATA FILE SERIES:ZNSH2.EMF                          ZNSH2E.EMF
EQUILIBRIUM OF ZnS IN H2. ALDRICH GOLD LABEL ELEC.GRADE
DATA 21/11/86. FLOW RATE H2=90cc/min. Pt:Pt13%Rh.
No. OF DATA POINTS=   FOR ZINC BLENDE. CAHN R100 USED.
DIMENSION OF RE-ENTRANT CAPILLARY CHANNEL:
LENGTH L2     = 1.9788 +/- 0.0182cm.
RADIUS R2     = 0.0574 +/- 0.0012cm.
b CORRECTION = 1.0000

RUN       EMF      TEMP C  -InW     PRESSURE
 1         9.010  884.823 23.3125  756.620
 2         9.010  884.823 23.2851  756.620
 3         9.010  884.823 23.3107  756.670
 4         9.010  884.823 23.2980  756.720      ROGUE VALUES
 6         9.010  884.823 23.3737  756.820      5  9.010 23.2319 756.
 7         9.010  884.823 23.3618  756.920      24 7.203 25.6133 772.
 8         8.651  856.423 23.7464  756.580      25 7.203 25.6643 768.
 9         8.651  856.423 23.7270  756.330      26 9.448 23.0061 767.
10         8.651  856.423 23.6719  755.890
11         8.651  856.423 23.6334  755.550
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12       8.651  856.423 23.7842  755.200
13       8.651  856.423 23.7270  754.860
14       8.651  856.423 23.7323  754.510
15       8.651  856.423 23.7144  754.170
16       8.651  856.423 23.7305  754.170
17       8.088  811.278 24.4638  756.420
18       8.088  811.278 24.4021  758.670
19       8.088  811.278 24.3580  760.920
20       7.706  780.205 24.8568  766.550
21       7.706  780.205 24.8491  772.190
22       7.706  780.205 24.8374  777.820
23       7.203  738.711 25.5671  777.820
27       9.448  919.087 22.8797  767.770
28       9.448  919.087 22.9084  767.770
29       9.448  919.087 22.9071  767.770
30       9.868  951.562 22.5485  767.770
31       9.868  951.562 22.5170  767.770
32       9.868  951.562 22.4721  767.770
33       9.868  951.562 22.4928  767.770
34      10.266  982.006 22.1294  767.770
35      10.266  982.006 22.1526  767.770
36      10.266  982.006 22.1469  767.770
37      10.266  982.006 22.1352  767.770
 5       9.010  884.823 23.2319  756.770
24       7.203  738.711 25.6133  772.970
25       7.203  738.711 25.6643  768.120
26       9.448  919.087 23.0061  767.770
 0       0.000    0.000  0.0000    0.000
         mV       C      In(Kg/s) mmHg
DATA FILE SERIES:ZNSH2.EMF                          ZNSH2F.EMF
EQUILIBRIUM OF ZnS IN H2. ALDRICH GOLD LABEL ELEC.GRADE
DATE 4/12/86. FLOW RATE H2=90cc/min. Pt:Pt13%Rh.
No. OF DATA POINTS=  FOR WURTZITE. CAHN R100 USED.
DIMENSION OF RE-ENTRANT CAPILLARY CHANNEL:
LENGTH L2     = 1.9788 +/- 0.0182cm.
RADIUS R2     = 0.0574 +/- 0.0012cm.
b CORRECTION = 1.0000

RUN      EMF     TEMP C  -InW    PRESSURE
 1      10.944 1033.168 21.5925  767.820
 2      10.944 1033.168 21.5849  767.820
 3      10.944 1033.168 21.5849  767.820
 4      10.944 1033.168 21.5849  767.820
 5      10.944 1033.168 21.5811  767.820
 6      10.944 1033.168 21.5849  767.820
 7      10.944 1033.168 21.5811  767.820
 8      10.944 1033.168 21.5811  767.820
 9      10.944 1033.168 21.5811  767.820
11      10.944 1033.168 21.5925  767.820
12      10.944 1033.168 21.6074  767.820
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13      12.822 1170.705 20.3001  767.820
14      12.822 1170.705 20.2848  767.820
15      12.822 1170.705 20.2612  767.820
16      12.822 1170.705 20.2785  767.820
17      12.822 1170.705 20.2549  767.820
18      12.822 1170.705 20.2596  767.820
19      12.822 1170.705 20.2322  767.820
20      12.822 1170.705 20.2404  767.820
21      12.822 1170.705 20.2596  767.820
22      12.822 1170.705 20.3032  767.820
23      12.822 1170.705 20.3153  767.820
24      12.560 1151.859 20.4613  767.820
25      12.560 1151.859 20.4396  767.820
26      12.560 1151.859 20.4396  767.820
27      12.560 1151.859 20.4554  767.820
28      12.560 1151.859 20.4515  767.820
29      12.560 1151.859 20.4455  767.820
30      12.560 1151.859 20.4396  767.820
31      12.560 1151.859 20.4455  767.820
32      12.302 1133.197 20.6355  767.820
33      12.302 1133.197 20.6421  767.820
34      12.302 1133.197 20.6135  767.820
35      12.302 1133.197 20.6135  767.820
36      12.302 1133.197 20.6157  767.820
37      12.302 1133.197 20.6201  767.820
38      12.302 1133.197 20.6135  767.820
39      12.302 1133.197 20.6377  767.820
40      12.302 1133.197 20.6179  767.820
41      12.302 1133.197 20.6179  767.820
42      11.911 1104.713 20.8888  767.820
43      11.911 1104.713 20.8888  767.820
44      11.911 1104.713 20.8905  767.820
45      11.911 1104.713 20.8837  767.820
46      11.911 1104.713 20.8854  767.820
47      11.911 1104.713 20.8989  767.820
48      11.911 1104.713 20.8595  767.820
49      11.911 1104.713 20.8871  767.820
50      11.911 1104.713 20.8854  767.820
51      11.522 1076.125 21.1680  766.620
52      11.522 1076.125 21.1718  766.620
53      11.522 1076.125 21.1775  766.620
54      11.522 1076.125 21.1699  766.620
55      11.522 1076.125 21.1851  766.620
56      11.522 1076.125 21.1718  766.620
57      11.104 1045.118 21.4878  766.620
58      11.104 1045.118 21.4850  766.620
59      11.104 1045.118 21.4989  766.620
60      11.104 1045.118 21.4850  766.620
61      11.104 1045.118 21.4850  766.620
62      11.104 1045.118 21.4878  766.620
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63       11.104 1045.118 21.4934  766.620
64       11.104 1045.118 21.4906  766.620
65       11.104 1045.118 21.4822  766.620
66       11.104 1045.118 21.4934  766.620
68       10.946 1033.317 21.6074  766.620
69       10.946 1033.317 21.6185  766.620
70       10.946 1033.317 21.6185  766.620
71       10.946 1033.317 21.6259  766.620
72       10.946 1033.317 21.6111  766.620
73       10.946 1033.317 21.6000  766.620
74       10.946 1033.317 21.6111  766.620
75       10.946 1033.317 21.6295  766.620
 0       0.000     0.000  0.0000    0.000
         mV       C      In(Kg/s) mmHg
DATA FILE SERIES:ZNSH2.EMF                      ZNSH2G.EMF
EQUILIBRIUM OF ZnSIN H2. ALDRICH GOLD LABEL ELEC.GRADE
DATE 9/12/86. FLOW RATE H2=90cc/min. Pt:Pt13%Rh.
No. OF DATA POINTS=46 FOR WURTZITE. CAHN R100 USED.
DIMENSION OF RE-ENTRANT CAPILLARY CHANNEL:
LENGTH L2     = 1.9788 +/- 0.0182cm.
RADIUS R2     = 0.0574 +/- 0.0012cm.
b CORRECTION = 1.0000  INTERNAL PRESSURE=3.02mmHg.

RUN      EMF     TEMP C  -InW    PRESSURE
14       12.563 1152.076 20.4215  765.270
15       12.563 1152.076 20.4154  765.270       EQUILIBRIA OF BALANC
16       12.563 1152.076 20.4174  765.270       AND SAMPLE NOT REACH
17       12.563 1152.076 20.4195  765.270       ROGUE VALUES:
18       12.563 1152.076 20.4113  765.270        1  12.852 20.4051
19       12.563 1152.076 20.4154  765.270        2  12.852 20.4072
20       12.563 1152.076 20.4215  765.270        3  12.852 20.3324
21       12.303 1133.270 20.6129  765.270        4  12.852 20.2940
22       12.303 1133.270 20.5909  765.270        5  12.852 20.2824
23       12.303 1133.270 20.5649  765.270        6  12.852 20.2731
24       12.303 1133.270 20.5909  765.270        7  12.852 20.2636
25       12.303 1133.270 20.5994  765.270        8  12.852 20.2565
26       12.303 1133.270 20.5770  765.270        9  12.852 20.2517
27       12.303 1133.270 20.5977  765.270        10 12.852 20.2420
28       12.303 1133.270 20.5840  765.270        11 12.563 20.4436
29       12.303 1133.270 20.5909  765.270        12 12.563 20.4356
30       12.303 1133.270 20.6179  765.270        13 12.563 20.4255
31       10.981 1035.936 21.5382  765.270
32       10.981 1035.936 21.5540  765.270     HISTORY OF SAMPLE
33       10.981 1035.936 21.5540  765.270     CONTINUE FROM ZNSH2F.EM
34       10.981 1035.936 21.5382  765.270     (EXPOSED TO H2 1170C)
35       10.981 1035.936 21.5618  765.270     BAKED IN ARGON AT 1034C
36       10.981 1035.936 21.5579  765.270     FOR SEVERAL DAYS
37       10.981 1035.936 21.5461  765.270     (MAY FORM OXIDE COATING
38       10.981 1035.936 21.5017  765.270     COOLED TO ROOM TEMP
39       10.981 1035.936 21.6111  765.270     WURTZITE METASTABLE
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40       10.981 1035.936 21.6111  765.270
41       11.521 1076.052 21.2402  765.270     REPEATED ZNSH2F.EMF EXP
42       11.521 1076.052 21.2020  765.270
43       11.521 1076.052 21.1563  765.270     Q. DOES POSSIBLE OXIDE
44       11.521 1076.052 21.1347  765.270     CAUSE KINECTIC HINDERAN
45       11.521 1076.052 21.1387  765.270     TO SAMPLE?
46       11.521 1076.052 21.1287  765.270     Q. DOES COOLING SAMPLE
47       11.521 1076.052 21.1347  765.270     ROOM TEMP AND REHEATING
48       11.521 1076.052 21.1287  765.270     1178C INDUCE IRREVERSIB
49       11.908 1104.494 20.8021  765.270     POLYTYPES OF SPHALERITE
50       11.908 1104.494 20.8871  765.270     OR WURTZITE TO EFFECT
51       11.908 1104.494 20.8989  765.270     VAPOUR PRESSURE OF SAMP
52       11.908 1104.494 20.9155  765.270     AND ULTIMINATELY ITS
53       11.138 1047.651 21.5262  765.270     FREE ENERGY OF VAPOURIS
54       11.138 1047.651 21.4421  765.270
55       11.138 1047.651 21.4214  765.270     ANS. HYDROGEN WILL
56       11.138 1047.651 21.4303  765.270     REMOVES ANY POSSIBLE OX
57       11.138 1047.651 21.4362  765.270     FORMATION.
58       11.138 1047.651 21.4362  765.270     ANS. NO.
59       11.138 1047.651 21.4244  765.270
60       11.138 1047.651 21.4362  765.270
 0       0.000     0.000  0.0000    0.000
         mV       C      In(Kg/s) mmHg
```

```
DATA FILE SERIES:ZNSHCLaa.EMF                        ZNSHCLA.EMF
SPHALERITE ZnS + HCl in Ar . 25/6/85.
FLOW RATES:HCl = 6.0cc/min &  Ar = 90.086cc/min.
No. OF DATA POINTS= 63. CAHN R100. TC Pt:Pt13%Rh.
DIMENSIONS OF CAPILLARY CHANNEL:
LENGTHS L1 = 0.0663+/-0.0052cm  L2 = 1.7936+/-0.0077cm
RADII   R1 = 0.0774+/-0.0045cm  R2 = 0.0559+/-0.0028c.
beta corr [1+(R2.L1/R1.L2)] = 1.0267. E=0.06244

RUN      EMF     TEMP C  -InW    PRESSURE
 7        9.288  906.618 23.1475  766.765
 8        9.289  906.696 23.3571  767.065 RUNS 1-6 ABORTED. HCl
 9        9.291  906.853 23.4890  767.365 BLOCKAGE.
10        9.288  906.618 23.4667  767.740
11        9.441  918.542 23.0800  768.090 Temperature range
12        9.442  918.620 23.2681  768.540  739-993C
13        9.441  918.542 23.4603  768.940
14        9.441  918.542 23.4445  769.040
15        9.441  918.542 23.1245  768.815
16        9.718  940.005 23.1412  768.715
17        9.719  940.082 23.1854  768.515
18        9.718  940.005 23.2908  768.465
19        9.718  940.005 23.3100  768.440
20        9.718  940.005 23.2137  768.565
21       10.014  962.766 23.1516  768.915
22       10.013  962.689 23.2290  768.965
23       10.013  962.689 23.0765  769.015
24       10.013  962.689 23.4281  769.290
25       10.015  962.842 23.2048  769.340
26       10.011  962.536 23.1700  769.290
27       10.288  983.679 23.0972  769.315
28       10.287  983.604 23.0545  769.215
29       10.290  983.831 23.0284  769.215
30       10.288  983.679 22.9992  769.215
31       10.404  992.489 23.0913  767.540
32       10.403  992.413 23.0311  768.290
33       10.404  992.489 23.0406  768.740
34       10.404  992.489 23.1019  766.715
35       10.178  975.301 23.1114  766.165
36       10.177  975.225 23.0118  765.815
37       10.177  975.225 23.0216  765.790
38       10.173  974.920 23.0663  765.790
39        8.726  862.380 23.6950  770.540
40        8.727  862.459 23.6729  771.040
41        7.246  742.285 24.7365  767.290
42        7.242  741.953 24.6450  765.740
43        7.242  741.953 24.6968  768.540
44        7.242  741.953 24.6823  769.815   RUNS 45-47 ABORTED
48        7.637  774.553 24.4490  768.390  BLOCKED HCL RUBY FLOAT
49        7.634  774.307 24.5299  766.715
```

```
50        7.630  773.979 24.4465  767.540
51        8.043  807.638 24.1169  770.265
52        8.044  807.718 24.1955  772.140
53        8.044  807.718 24.1411  772.315
54        8.041  807.476 24.0866  772.290
55        8.459  841.111 23.9137  771.540
56        8.459  841.111 23.8586  770.415
57        8.460  841.191 23.8380  769.540
58        8.736  863.173 23.7580  768.490
59        8.736  863.173 23.7601  767.240
60        8.736  863.173 23.7137  765.440
61        9.158  896.447 23.4692  763.965
62        9.158  896.447 23.4972  762.915
63        9.157  896.369 23.4616  762.015
64        9.588  929.952 23.3468  761.715
65        9.588  929.952 23.3047  759.540
66        9.589  930.029 23.3379  759.290
67       10.009  962.383 23.1637  759.190
69       10.011  962.536 23.1758  758.540   RUN 68 DELETED(CURVED LI
70       10.011  962.536 23.1610  758.590
71       10.432  994.612 23.0677  758.840
72       10.433  994.688 23.0048  758.990
73       10.433  994.688 22.9268  759.290
 0       0.000     0.000  0.0000    0.000
         mV      C        In(Kg/s) mmHg
```

```
DATA FILE SERIES:ZNSHCLbb.EMF                       ZNSHCLb.EMF
SPHALERITE ZnS + HCl in Ar . 29/6/85.
FLOW RATES:HCL = 10.0cc/min & Ar = 90.086cc/min.
No. OF DATA POINTS = 42. CAHN R100. TC Pt:Pt13%Rh.
DIMENSIONS OF CAPILLARY CHANNEL:
LENGTHS L1 = 0.0663+/-0.0052cm  L2 = 1.7936+/-0.0077cm.
RADII   R1 = 0.0774+/-0.0045cm  R2 = 0.0559+/-0.0028cm.
beta corr  = 1.0267.            E  = 0.0999

RUN     EMF    TEMP C  -InW    PRESSURE
 1     10.142  972.554 22.8167  764.830
 2     10.129  971.562 22.8639  764.830 RUN 1 = RUN 3.5 ORIGINAL
 3     10.141  972.478 22.7451  765.355 RUN 1 ABORTED-MEM RIG NOT
 4     10.145  972.783 22.8053  766.155 NOT SETTLED DOWN
 5     10.144  972.706 22.8344  766.480
 6     10.393  991.655 22.6655  766.780 Temperature Range
 7     10.392  991.579 22.6216  766.705  741-993C
 8     10.392  991.579 22.6584  766.880
 9     10.392  991.579 22.6818  767.155
10     10.392  991.579 22.6114  767.580
11      9.724  940.468 22.8220  768.030
12      9.725  940.545 22.8768  768.130
13      9.724  940.468 22.8254  768.030
14      9.720  940.159 22.8921  768.030
15      9.426  917.376 23.0223  768.180
16      9.430  917.687 22.9665  768.330
17      9.431  917.765 23.0355  768.455
18      9.429  917.609 22.9910  768.205
19      9.428  917.531 23.0159  767.930
20      9.017  885.374 23.1386  767.330
21      9.013  885.059 23.1019  767.330
22      9.013  885.059 23.2137  767.505
23      9.013  885.059 23.1663  767.880
24      8.316  829.652 23.5400  768.030
25      8.315  829.572 23.5273  768.230
26      8.315  829.572 23.5022  768.305
27      8.584  851.090 23.4371  768.230
28      8.583  851.010 23.2643  768.580
29      8.582  850.930 23.3737  769.305
30     10.285  983.451 22.6845  769.805
31     10.270  982.310 22.7173  770.105
32      7.252  742.783 24.2511  766.730
33      7.250  742.617 24.2439  767.330
34      7.250  742.617 24.4927  767.930
35      7.251  742.700 24.2170  767.930
36      7.629  773.896 24.0568  763.430
37      7.628  773.814 24.0272  761.805
38      7.625  773.568 24.0203  761.380
39      8.185  819.111 23.6328  760.130
40      8.186  819.191 23.6192  759.980

41        8.188  819.353 23.6317   759.580
42        8.187  819.272 23.6250   758.255
 0       0.000     0.000  0.0000     0.000
         mV        C      In(Kg/s) mmHg
```

```
DATA FILE SERIES:ZNSHCLee.EMF                           ZNSHCLe.emf
SPHALERITE ZnS + HCl in Ar(RGP4). 6/8/86
FLOW RATES: HCl = 9.0cc/min & Ar = 84.0cc/min. Ar MFC Used.
No. OF DATA POINTS = 47. CAHN R100 USED. TC Pt:Pt13%Rh.
DIMENSIONS OF CHANNEL:
LENGTH L2 = 2.1008cm
RADIUS R2 = 0.0560cm
beta corr = 1.000E0       E = 0.0989

RUN      EMF    TEMP C  -InW    PRESSURE
 1      7.865  793.184 24.0497  764.540
 2      7.865  793.184 23.8579  764.540  Temperature range
 3      7.865  793.184 23.9381  764.540   766-993C
 4      7.865  793.184 23.8179  764.540
 5      7.865  793.184 23.8631  764.540
 6      7.865  793.184 23.9162  764.540
 7      7.865  793.184 23.8394  765.240
 8      7.509  764.034 24.0003  765.240
 9      7.509  764.034 24.1432  765.240
10      7.509  764.034 24.0367  765.240
11      7.502  763.458 24.1124  765.240
12      8.251  824.427 23.7540  765.240
13      8.251  824.427 23.7089  765.240
14      8.251  824.427 23.6844  765.240
15      8.251  824.427 23.6618  765.240
16      8.251  824.427 23.7327  765.240
17      8.251  824.427 23.6894  765.240
18      8.251  824.427 23.6769  765.240
19      8.251  824.427 23.6906  765.240
20      8.251  824.427 23.6819  765.240
21      8.251  824.427 23.6906  765.740
22      8.649  856.264 23.5571  765.740
23      8.649  856.264 23.5226  765.740
24      8.649  856.264 23.5049  765.740
25      8.649  856.264 23.4499  765.740
26      8.649  856.264 23.5149  765.740
27      9.055  888.362 23.3392  765.740
28      9.055  888.362 23.3779  765.740
29      9.055  888.362 23.2498  765.740
30      9.055  888.362 23.3166  765.740
31      9.055  888.362 23.3193  765.740
32      9.441  918.542 23.2989  762.490
33      9.441  918.542 23.1372  762.490
34      7.405  755.456 24.2315  762.490
35      7.405  755.456 24.1733  762.490
36      7.405  755.456 24.2234  762.490
37      7.405  755.456 24.2152  762.490
38      9.978  960.007 22.9520  762.490
39      9.978  960.007 23.0515  762.490
40      9.978  960.007 22.9844  762.490

41      9.978  960.007 22.9383  762.490
42      9.978  960.007 22.9712  762.490
43     10.377  990.440 22.8501  766.040
44     10.377  990.440 22.8254  766.040
45     10.377  990.440 22.8400  766.040
46     10.377  990.440 22.8032  766.040
47     10.377  990.440 22.8713  766.040
 0      0.000    0.000  0.0000    0.000
        mV     C        In(Kg/s) mmHg
```

```
DATA FILE SERIES:ZNSHCLff.EMF                  ZNSHCLf.EMF
SPHALERITE ZnS + HCl in Ar(RGP4). 19/8/86
FLOW RATES: HCl = 6.0cc/min & Ar = 84.0cc/min. Ar MFC Used.
No. OF DATA POINTS = 47. CAHN R100 USED. TC Pt:Pt13%Rh.
DIMENSIONS OF CHANNEL:
LENGTH L2 = 2.1008cm
RADIUS R2 = 0.0560cm
beta corr = 1.000E0    E = 0.0667

RUN     EMF    TEMP C  -InW    PRESSURE
 1     10.379  990.593 23.1981  770.250
 2     10.379  990.593 23.0928  770.250  Temperature range
 3     10.379  990.593 23.1193  770.250   766-993C
 4     10.379  990.593 23.1308  770.250
 5     10.379  990.593 23.1111  770.250
 6     10.379  990.593 23.0928  770.250
 7      9.986  960.620 23.3431  770.250
 8      9.986  960.620 23.2796  770.250
 9      9.986  960.620 23.3418  770.250
10      9.986  960.620 23.2176  770.250
11      9.986  960.620 23.2851  770.250
12      9.986  960.620 23.2570  770.250
13      9.986  960.620 23.2754  770.250
14      9.986  960.620 23.2976  770.250
15      9.986  960.620 23.2570  770.250
16      9.986  960.620 23.2426  770.250
17      9.986  960.620 23.2087  770.250
18      9.331  909.975 23.4918  770.250
19      9.331  909.975 23.5244  770.250
20      9.331  909.975 23.6136  770.250
21      9.331  909.975 23.4858  770.250
22      9.331  909.975 23.5038  770.250
23      9.331  909.975 23.6190  770.250
24      9.331  909.975 23.5098  770.250
25      9.331  909.975 23.4873  770.250
26      9.331  909.975 23.5008  770.250
27      8.684  859.045 23.7563  770.250
28      8.684  859.045 23.7848  770.250
29      8.684  859.045 23.7270  766.680
30      8.684  859.045 23.8314  765.550
31      8.684  859.045 23.7505  764.430
32      8.684  859.045 23.7876  762.780
33      8.684  859.045 23.7059  761.050
34      8.684  859.045 23.8125  761.050
35      8.684  859.045 23.7792  760.000
36      7.909  796.764 24.2984  758.800
37      7.900  796.032 24.1423  758.800
38      7.900  796.032 24.1771  758.800
39      7.900  796.032 24.2883  761.900
40      7.900  796.032 24.1344  763.830

41      7.900  796.032 24.3233  765.770
42      7.900  796.032 24.1384  767.700
43      7.546  767.079 24.4111  767.700
44      7.546  767.079 24.4723  767.700
45      7.546  767.079 24.4179  767.700
46      7.546  767.079 24.5077  767.700
47      7.546  767.079 24.4021  767.700
 0     0.000     0.000  0.0000    0.000
       mV      C        In(Kg/s) mmHg
```

```
DATA FILE SERIES:ZNSHCLhh.EMF                          ZNSHCLh.EMF
SPHALERITE ZnS + HCl in Ar(RGP4). 16/1/87.
FLOW RATES: HCl = 8.64cc/min & Ar = 90.0cc/min. Ar MFC Used.
No. OF DATA POINTS = 30. CAHN R100 USED. TC Pt:Pt13%Rh.
DIMENSIONS OF CHANNEL:
LENGTH L2 = 1.9788cm
RADIUS R2 = 0.0574cm
beta corr = 1.000E0      E = 0.0876

RUN      EMF     TEMP C  -InW    PRESSURE
 2        7.870  793.591 23.9955  775.250
 3        7.870  793.591 23.9817  775.250 Temperature range
 4        7.870  793.591 23.9921  775.250  752-979C
 5        7.870  793.591 23.9748  775.250
 6        7.870  793.591 23.9955  775.250
 7        7.870  793.591 24.0291  775.250
 8        8.264  825.473 23.8125  775.250
 9        8.264  825.473 23.7960  775.250
10        8.264  825.473 23.7876  775.250
11        9.053  888.205 23.4790  775.250
12        9.053  888.205 23.4858  775.250
13        9.053  888.205 23.4452  775.250
14        9.053  888.205 23.4488  775.250
15        9.053  888.205 23.4476  775.250
16        9.053  888.205 23.4452  775.250
17        9.433  917.920 23.2976  779.200
18        9.433  917.920 23.2907  779.200
19        9.433  917.920 23.2982  779.200
20        9.433  917.920 23.2962  779.200
21        9.829  948.561 23.1527  780.700
22        9.829  948.561 23.1259  780.700
23        9.829  948.561 23.1623  780.700
24       10.216  978.198 23.0302  780.900
25       10.216  978.198 23.0097  780.900
26       10.216  978.198 22.9850  780.900
27       10.216  978.198 23.0036  780.900
28        7.370  752.563 24.2686  780.900
29        7.370  752.563 24.3674  780.900
30        7.370  752.563 24.3484  780.900
31        7.370  752.563 24.3068  780.900
 0       0.000     0.000 0.0000     0.000
         mV      C       In(Kg/s) mmHg
```

```
DATA FILE SERIES:ZNSHCLii.EMF                          ZNSHCLi.EMF
SPHALERITE ZnS + HCl in Ar(RGP4). 23/1/86
FLOW RATES: HCl = 5.83cc/min & Ar = 91.0cc/min. Ar MFC Used.
No. OF DATA POINTS = 21. CAHN R100 USED. TC Pt:Pt13%Rh.
DIMENSIONS OF CHANNEL:
LENGTH L2 = 1.9788cm
RADIUS R2 = 0.0574cm
beta corr = 1.000E0      E = 0.0602

RUN      EMF     TEMP C  -InW    PRESSURE
 1        7.372  752.729 24.6971  769.000
 2        7.372  752.729 24.6937  767.360  Temperature range
 3        7.372  752.729 24.6886  765.720   752-979C
 4        7.372  752.729 24.6627  764.080
 5        7.713  780.778 24.4960  762.430
 6        7.713  780.778 24.4566  760.790
 7        7.713  780.778 24.4723  759.150
 8        8.504  844.708 24.0467  759.830
 9        8.504  844.708 24.0043  760.500
10        8.504  844.708 24.0786  761.250
11        9.026  886.082 23.8125  762.000
12        9.026  886.082 23.7993  762.750
13        9.026  886.082 23.7792  763.500
14        9.026  886.082 23.7689  764.250
15        9.823  948.099 23.4888  764.250
16        9.823  948.099 23.4858  764.250
17        9.823  948.099 23.4550  764.250
18       10.212  977.894 23.3471  764.250
19       10.212  977.894 23.3193  764.250
20       10.212  977.894 23.3233  764.250
21       10.212  977.894 23.3587  764.250
 0       0.000     0.000 0.0000     0.000
         mV      C       In(Kg/s) mmHg
```

```
DATA FILE SERIES:ZnCl22NH3B.EMF
EQUILIBRIUM OF DIAMMINEDICHLOROZINC(II) IN ARGON. 18/5/87.
FLOW OF ARGON        = 90cc/min. TC TYPE K  NiCr:NiAl.
No. OF DATA POINTS = 43 . CAHN R100 ELECTROBALANCE USED.
DIMENSIONS OF RE-ENTRANT CAPILLARY CHANNEL:
LENGTH L2            = 1.8512 +/- 0.0032 cm
RADIUS R2            = 0.0542 +/- 0.0017 cm
beta correction      = 1.000   Internal Pressure = 5.00mmHg.

RUN      EMF    TEMP K  -InW     PRESSURE
 1       9.281  501.15  22.3129  762.40
 2       9.281  501.15  22.4425  762.40    Initial Wt 231.4mg
 3       9.281  501.15  22.4928  762.40    runs 1-4 invalid
 4       9.281  501.15  22.5309  762.40
 5       9.281  501.15  22.5542  762.40
 6       9.281  501.15  22.5920  762.40
 7       8.110  472.15  24.5938  772.10
 8       8.110  472.15  24.6521  772.10
 9       8.110  472.15  24.5259  772.10
10       8.110  472.15  24.6069  772.10
11       6.815  439.15  26.7272  776.45
12       7.428  455.15  25.8357  776.45
13       7.428  455.15  25.7458  776.45
14       7.428  455.15  25.6871  776.45
15       8.845  490.15  23.6400  776.45   WEIGTH LOSS
16       9.680  511.15  22.9800  776.45    9.4 mg
17       9.680  511.15  23.2143  776.45
18       9.680  511.15  23.5144  776.45   12.7 mg
19       9.680  511.15  23.7172  776.45
20      10.038  520.15  23.5623  776.45   14.3 mg
21      10.915  541.15  23.3260  769.40
22      10.915  541.15  23.5553  769.40
23      10.915  541.15  23.8234  769.40
24      10.915  541.15  24.0774  769.40
25      10.915  541.15  24.2712  769.40
26      10.915  541.15  24.4378  769.40
27      10.915  541.15  24.7172  769.40
28      10.915  541.15  24.9669  769.40    21.5 mg
29      11.726  561.15  24.4995  769.40
30      11.726  561.15  24.7595  769.40
31      11.726  561.15  24.9447  769.40
32      11.726  561.15  25.2330  768.15    24.7 mg
33      12.516  582.15  24.6574  768.15
34      12.516  582.15  24.9460  768.15
35      12.516  582.15  25.1665  768.15
36      12.516  582.15  25.4037  768.15
37      16.306  672.15  23.3652  768.15
38      16.306  672.15  23.5985  768.15
39      16.306  672.15  23.8644  768.15
40      16.306  672.15  24.1205  768.15
```

```
41      16.306  672.15  24.3412  768.15
42      16.306  672.15  24.6835  768.15
43      16.306  672.15  24.9287  768.15
44      16.306  672.15  25.6429  768.15
45      16.306  672.15  26.0675  768.15    38.7 mg
 0       0.000    0.00   0.0000    0.00
        mV      K       In(Kg/s) mmHg
```

ERRATA

pp. 18/19.		List of tables - reversed pages.
p. 20,	l. 20.	For "lead" read "led".
p. 21,	l. 14.	For "have" read "has".
p. 31,	l. 18.	For "vapour of" read "vapour at".
p. 37,	l. 10 & 13.	For "appendeces" read "appendices".
p. 42,	l. 1.	For "capusle" read "capsule".
p. 42,	l. 12.	For "This 're-entrant' capsule" read "The inclusion of a 're-entrant' capillary ".
p. 43,	l. 4.	For "micros" read "microns".
p. 43,	l. 10.	For "from a" read "from a corresponding".
p. 43,	l. 22.	For "laminor" read "laminar".
p. 44,	l. 20.	For "waded" read "weighted".
p. 45,	l. 3.	For "has" read "is".
p. 47,	l. 15 & 16.	For "hours table" read "hours. Table".
p. 51,	l. 12.	For "understudy" read "under study".
p. 52,	l. 3.	For "Linott" read "Lintott".
p. 58,	l. 14.	For "applys" read "applies".
p. 59,	l. 7.	For "filteration" read "filtration".
p. 74,	l. 7.	For "Bettelheim" read "Bettelheim[17]".
p. 74,	l. 17.	For "to be" read "to be the following".
p. 74,	l.18 to 21.	For "(i),(ii) and (iii)" read "Purified $ZnCl_2$ was dissolved in absolute ethanol and gaseous dried ammonia was then bubbled *through the solution, when crystals of* $ZnCl_2(NH_3)_2$ precipitated.".
p. 87,	l. 21.	For "from" read "for".
p. 92,	l. 7.	For "of the nature" read "on the nature".
p. 94,	l. 22.	For "formation" read "formulation".
p. 95,	l. 9.	For "Berthalot" read "Berthelot".
p. 96,	l. 13.	For "diatomic" read "diatomic species".
p. 108,	l. 3.	For "similarly" read "close".
p. 113,	l. 7.	For "is" read "in".
p. 114,	l. 21.	For "logartithmic" read "logarithmic".
p. 120,	l. 18.	For "28.3T" read "$28.3T\log_{10}T$".
p. 122,	l. 5.	For "baking" read "baking of".
p. 131,	l. 18.	For "are" read "is".
p. 137,	l. 7.	For "Robertons" read "Robertson".
p. 138,	l. 1.	For "However" read "However in".
p. 139,	l. 5.	For "makes" read "make".
p. 139,	l. 9.	For "and" read "or".
p. 140,	l. 9.	For "indirect" read "in direct".
p. 141,	l. 22	For sentence "On closer ... each other" read "Close inspection of MS results of Schafer[11] and Rice[4] reveals good agreement for the relative ionisation intensity ratio for $ZnCl_2^+$: $ZnCl^+$: Zn^+, i.e., 100:13:7 and 100:11:6 respectively.".
p. 152,	l. 7.	For "177.5" read "117.5".
p. 170,	l. 27.	For "by" read "by elementary analyses on the heated samples (see table 5.1).".
p. 179,	l. 1 & 3.	For "give ... entropy" read " , the following enthaply and entropy changes may be derived.".
p. 186,	l. 12.	For "196.5" read "196.3".
p. 193,	l. 10.	For "in" read "as in".
p. 206,	l. 15.	For "appendeces" read "appendices".