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STUDIES IN THE HIGH TEMPERATURE CHEMICAL REACTIONS INVOLVING

[A] METAL HALIDE - METAL AND METAL HALIDE - METAL OXIDE EQUILIBRIA

[B] CERIUM SULPHIDE (Ce_2S_3) AND NICKEL CHLORIDE

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Section II : Equilibrium study of the reaction Nl(e) + $NiCl_2(g)$ = 2NiCl(g)

Section II : Reaction of nickel dichloride with molten aluminium

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CHAPTER - 1

INTRODUCTION

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INTRODUCTION

1.1. GENERAL

Research in high temperature chemistry has started gaining ground not probably before 1950. Brewer[1] has aptly defined "High temperature chemistry as the chemistry of the systems at sufficiently high temperatures so that the oxidation states, compounds and general chemical behaviour differ appreciably from that at the room temperatures." In the course of the last two decades considerable advancement has been made in the study of thermodynamics and kinetics of high temperature processes. Prior to that this area of specialisation have been studied by a few metallurgists and ceramists. The need for high temperature materials having sufficient resistance to corrosion, thermal shocks, mechanical strength during extreme operating conditions in the fast developing modern industry has given a good impetus for the study of high temperature processes. High temperatures can be produced by several methods viz; electrical resistance, flames, arcs and discharges, solar furnace, nuclear fusion and atomic fission. Extremely high temperatures (of the order of 10^6 to 10^8) are produced by atomic fission and nuclear fusion. Employing chemical reactions[2] temperatures upto 6000°K can be obtained. At these very high temperatures it is possible to get large concentrations of atoms and molecules in the ionic state. Thus the existence of various kinds of odd molecules electron deficient and with non-localized bonding are common at high temperatures. Mass spectrography and optical spectra have given spectacular results in identifying the gaseous species at high temperatures. Some of the important radicals identified are $(CH_3)_2N$, CS, CCl_2, CS_2, AlCl, AlF, BeCl, BeF, $(BOCl)_3$, BeC_2, LaC_2, Ca_2C_2, BeOH, $Si(OH)_4$, Al_2O, AlO, ZrO, B_2O_2, SiO, Al_2C_2, C_2, C_3, TiO, MgF, SrF, CaH, CO, CN, OH, O, H, N, NH_2, CF, NiCl and CF_2, etc.

1.2 IMPORTANT HIGH TEMPERATURE REACTIONS

With the development of the high temperature reactions many new industrially as well as historically important processes are developed. Some of the metallurgical processes are the reduction, refining, annealing and heat treatment of pure metals and alloys for structural uses. Glass manufacturers and ceramists investigated high temperature phase relations to satisfy the demand for cheap containers, windows, insulators, refractories, etc. Flames and combustion processes at high temperatures have been studied for the conversion of heat energy to mechanical energy in engine designs, new fuels. These and many other such processes directed much thought to the high temperature and metallurgical research. A few examples of classical high temperature processes are:

a : Preparation of graphite from amorphous carbon.

b : Preparation of SiC and CaC_2.

c : Preparation of elementary phosphorous.

d : Preparation of Na and Al by high temperature electrolysis process.

and e : Cracking and polymerization of hydrocarbons.

Their efficiencies in many cases will be higher if they are operated at still higher temperatures.

1.3 CHEMICAL TRANSPORT REACTIONS

Possibilities of new and important materials depend directly on the existence of unusual species which can act as intermediates at high temperature. It is quite possible to obtain free radicals in thermodynamic equilibrium in high temperature systems. Their properties and stabilities can be studied and possibly they can even be condensed as new compounds. The intermediates can be obtained in two ways:

i) By directly heating the compounds and elements to higher and higher temperatures until they give unusual species with lower oxidation states e.g. AlO, ZrO, TiO, C_2, C_3, CN, Ba_2O, Ba_2O_2, BeO, B_2O_2, etc.

ii) Condensed phase or solid-liquid interactions e.g. metal-metal halide, metal halide-metal oxide metal halide-metal sulfide, metal-metal sulfide systems, etc. in which the species are NiCl, AlCl, AlF, AlOCl, LaS, CeS, BF, AlS, etc.

1.3.1 Definition of chemical transport

When nickel chloride vapour is passed over metallic nickel the equilibrium approached in the hot zone is:

$$Ni(s) + NiCl_2(g) = 2NiCl(g) \qquad ...[1]$$

and reverts on cooling to nickel and normal halide. Schäfer[3] in 1962 has named this type of heterogeneous reactions as chemical transport reactions. The formation of the subhalide helps to overcome the high energy barrier for the distillation of metal, by promoting it to vapour phase[4]. The term chemical transport reactions has, however, wide applications. Schäfer has defined these reactions as those in which a solid or liquid substance 'A' reacts with a gas 'B' to form exclusively vapour phase reaction products which in turn undergo the reverse reaction at a different place in the system resulting in the formation of 'A'. Substance 'A' however does not possess an appreciable vapour pressure at the applied temperatures and is transported chemically.

However, solid and liquid interactions can also give unstable vapour phase compounds, e.g. $Al_2O(g)$[5]

$$Al_2O_3(c) + Si(l) = SiO_2(c) + Al_2O(g) \qquad \ldots [2]$$

When a high boiling halide such as MgF_2 or CaF_2 is added to the aluminium containing material, aluminium will be produced through aluminium subhalide[6]

$$2Al(l) + MgF_2(c) \text{ or } CaF_2(c) = 2AlF(g) + Mg(g) \text{ or } Ca(g) \ldots [3]$$

In these cases both aluminium suboxide and subfluoride can be carried away from the hot zone by an inert gas.

Thus the chemical transport reactions also includes such reactions where a solid or liquid substance 'A' reacts either with a gas or liquid 'B' facilitating the transport of 'A' through the formation of an exclusively vapour phase compound which is unstable.

1.4 IMPORTANCE OF CHEMICAL TRANSPORT REACTIONS

Chemical transport reactions are very useful in chemistry, physics and industry. These reactions can be successfully utilized to grow single crystals, to promote solid state reactions for better results and in metallurgy to produce and refine metals, in the preparation of alloys, syntheses of new compounds, etc.

1.4.1 In Solid State Reactions

Reactions between the starting solid materials can be enhanced when solid substances are joined together by a transport reaction. It is interesting to note that in a whole series of reactions with solids as starting materials, it has been shown that a liquid or gas phase is involved as a reaction promoter[7], viz. the reaction between calcium and stannic oxides proceeds very rapidly when reducing agents such as H_2, CO and C are added[8, 9]

$$2CaO(c) + SnO_2(c) = Ca_2SnO_4(c) \qquad ...[4]$$

$$SrO(c) + SnO_2(c) = SrSnO_3(c) \qquad ...[5]$$

In this system the starting material need not be in contact with each other[8,10] since SnO_2 will be transported to the alkaline earth oxide via gaseous SnO.

$$SnO_2(c) + CO(g) = SnO(g) + Ca_2(g) \qquad ...[6]$$

$$SnO_2(c) + H_2(g) = SnO(g) + H_2O(g) \qquad ...[7]$$

One of the most important recent chemical transport reactions is the formation of aluminium carbide by the action of aluminium monochloride on carbon[11]

$$2Al(1) + AlCl_3(g) = 3AlCl(g) \qquad ...[8]$$

$$6AlCl(g) + 3C(c) = Al_4C_3 + 2AlCl_3(g) \qquad ...[9]$$

Heim[11] has not only prepared Al_4C_3 at temperatures 900-1300°C by the above method but also obtained it 95.8% pure.

Chemical transport reactions are also useful in preparing spinels $NiCr_2O_4$[12], $MgCr_2O_4$[13], $MgAl_2O_4$[14]. The formation of nickel aluminate($NiAl_2O_4$) through aluminium trichloride and nickel oxide has been discussed in this thesis (Chapter 4).

1.4.2 Advantages of transport reactions in solid state chemistry

(A) With the aid of transport reactions useful products of solid state reactions have been obtained at considerably lower temperatures e.g. the direct combination of aluminium and carbon gives aluminium carbide at 1700 to 1800° [14] whereas according to equation (9) the formation takes place at much lower temperatures 900°-1300° [11].

(B) It is not necessary to use stoichiometric mixtures as starting materials as is usually the case in solid state reactions. The composition of the final product is determined by quantitative analysis of the reaction products. This provides concrete information leading to the elucidation of the reaction mechanism.

(C) Experimental conditions can be chosen so that the constituent in excess can be removed by a transpiration after the conversion is complete. Thus the technique will be simple and the products will have high purity.

(D) The components of the reaction need not be mixed since one of them can be transported[8,10].

1.4.3. Hydrothermal chemistry

Analogous to solution chemistry at room temperatures, aqueous systems also exist at high temperatures. Research in this field is important for explaining geological phenomena for refining minerals and synthesis of perfect crystals[16]. The identification and chemical transport of the gaseous species $Si(OH)_4$[17], $Be(OH)_2$[18] and the hydroxides of zinc, tungsten[19] and boron[20] have provided methods for the removal of trace impurities[21].

1.4.4. Use of chemical transport reactions in metallurgy

Chemical transport reactions find applications in many places in metallurgy; a few very important uses are given below:

(A) Mond-Longer process

This process involving the reversibility of the reaction is used for refining nickel[22]. Finely powdered crude nickel when treated with carbon monoxide at 50° and atmospheric pressure evaporates as nickel carbonyl [$Ni(CO)_4$]. This gas which led into a decomposition tower decomposes to pure granular nickel.

(B) The importance of Boudard equilibrium is well-known for the reduction of metal oxides e.g. in the technical recovery of iron and zinc.

(C) The iodide method developed by Van Arkel[23] is very useful for the purification of metals. In this the crude metal is vaporized as iodide and is decomposed on a hot wire[24]

$$Zr(c) + 2I_2(g) = ZrI_4(g) \qquad ...[10]$$

$$ZrI_4(g) = Zr(c) + 4I(g) \qquad ...[10a]$$

(D) Under suitable conditions metals like iridium[25], platimum[26] and silver[27] can be removed and pure crystals can be grown by transporting them through a stream of oxygen

$$Ir(c) + 3/2\ O_2(g) = IrO_3(g) \qquad ...[11]$$

$$Pt(c) + O_2(g) = PtO_2(g) \qquad ...[12]$$

$$Ag(c) + 1/2\ O_2(g) = AgO(g) \qquad ...[13]$$

It is also possible to transport ruthemium, rhodium and palladium in chlorine atmosphere[28-30].

1.5. AIM AND OBJECTIVES OF THE PRESENT WORK

From the information given in the preceeding pages it may be observed that the chemical transport reactions involving metal halides play a very important role in understanding (a) the formation of subhalides with the same or different metals, (b) the formation of spinels and oxyhalides when they (the halide of metals) react with metallic oxides, (c) the formation of metals and pure chlorides of the other metal by reaction of these halides with other metal sulfides, and (d) the thermodynamic properties of the species involved. The present work, therefore, aims at studying the following reactions:

(1) Equilibrium study of the reaction of a metal with its halide:

$$Ni(c) + NiCl_2(g) = 2NiCl(g)$$

at high temperatures to determine the heat of reaction, entropy of reaction and thereby determining the entropy of NiCl(g) at the mean temperature. The experimental work is described in Chapter 3.

(2) Study of the reaction of aluminium trichloride gas with nickel oxide.

Reaction of aluminium trichloride gas with nickel oxide has been studied at high temperatures. In this reaction nickel aluminate spinel has been observed along with gaseous nickel dichloride and aluminum oxychloride according to the equation

$6NiO(c) + 4AlCl_3(g) = NiAl_2O_4(c) + 5NiCl_2(g) + 2AlOCl(g)$ ..[14]

A detailed study of this reaction is given in Chapter 4.

(3) The final chapter of the thesis deals with the study of the reactions of gaseous nickel dichloride with cerium sulfide and molten aluminium. Various reactions taking part are discussed.

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CHAPTER - 2

THERMODYNAMIC CONSIDERATIONS

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THERMODYNAMIC CONSIDERATIONS

2.1. THERMODYNAMIC STUDY

The main purpose of chemical thermodynamics is to predict chemical equilibria from the thermal data. This can be done for a given reaction only if the necessary information is available over the desired temperature range for every species participating in the reaction. Therefore, the evaluation and correlation of thermodynamic data are important aspects of chemical thermodynamics. A knowledge of thermodynamic quantities like heat of formation, enthalpy, entropy and free energy functions at different temperatures is finding ever increasing use in the science and technology for the determination of the stability of chemical substances, the position of equilibrium in chemical reactions and in the study of detailed structure and energetics of atoms, gaseous molecules, crystals, liquids, etc. Thermodynamic methods are thus useful in understanding many diverse phenomena.

The study of thermodynamics of high temperature reactions is based on the measurement of the equilibrium pressures of the constituents of the reaction. The study of vaporization process or the equilibrium of the chemical reaction helps to establish the nature and energetics of chemical binding in the gaseous state.

Gilles[31] has rightly emphasised the importance of the following points in the study of high temperature chemical reaction:

a : The net reaction is to be established.

b : The gaseous species are to be identified.

c : The vapour pressure is to be measured.

d : The kinetics may be studied.

e : Finally, the detailed mechanism of the reaction is to be established.

2.2. GENERALIZATIONS USEFUL IN HIGH TEMPERATURE REACTIONS

The following three generalizations are very helpful in predicting the gaseous products of an equilibrium reaction at high temperature. The first two are given by Brewer[32] and the third by Searcy[33]. In view of their importance in the present work they are stated below. Detailed discussion has been given in literature[34].

1) The higher the temperature of a gas-solid, or gas-liquid equilibrium, the more nearly equal will be the partial pressures of various species.

2) A gas will react only endothermically with a solid to produce a significant yield of the reaction product, if the reaction produces at least as many moles of gas as are consumed in the reaction.

3) All equilibrium reactions that yield products when the temperature is increased must be endothermic and must occur with an increase in entropy. This is known as the principle of successive entropy states.

2.3. METHODS FOR THE STUDY OF EQUILIBRIUM OF A REACTION

Experimental techniques for measuring the equilibrium vapour pressures directly and indirectly are described in detail by Margrave[35,36].

2.3.1. Equilibrium pressures by direct measurements

Direct static techniques for the vapour pressure measurements at fixed temperature in a closed vessel have been employed by utilizing various instruments from simple U tube manometers containing mercury or some other fairly non-volatile liquid for relatively high pressure determinations, to highly complex gauges that must be applied within certain pressure limits. Vapour density methods, sickle gauges, dew point method, boiling point method, are a few techniques for measuring vapour pressures directly. But in equilibrium reactions of the type $Ni + NiCl_2 = 2NiCl$, $Al(l) + NiCl_2(g) = 2AlCl(g) + Ni(c)$, it is difficult to determine the pressures by these methods due to the reactivity of the out coming gases.

2.3.2. Indirect measurement of vapour pressures

A simple, very useful and accurate method is the flow or transpiration method for the determination of vapour pressures greater than 10^{-3} atms. For measuring the pressures less than 10^{-3} atms., Langmuir, Knudsen effusion, torsion effusion, molecular flow effusion, optical spectroscopy and mass spectrometry are very useful.

Methods in which vapour pressures less
than 10^{-3} atms. are measured:

2.3.3 Langmuir free evaporation

This method has the advantage of minimizing sample contamination being experimentally simpler and capable of the measurement of low vapour pressures. Hence this is widely employed in the determination of the vapour pressures of refractory materials. The disadvantage in this method is that the pressure measured is not necessarily the equilibrium vapour pressure and that the vapour species must be identified independently.

2.3.4. The Knudsen effusion method

This method of measuring small vapour pressures is important for the determination of thermodynamic properties of vapours and condensed phases in equilibrium. The method is based on the kinetic theory of gases by which the molecular flux at a boundary can be calculated for a gas at equilibrium. In this technique the vapour of a single species in equilibrium with its condensed phase is allowed to flow from an isothermal container through a small thin edged orifice into an evacuated space.

The vapour pressures of the condensed phase is related by the effusion formula to the temperature T, the mass 'm' of a molecule in the vapour, the mass rate of effusion dw/dt, the orifice area A_o and the usual natural constants of kinetic theory. Thus for the steady state effusion:

$$P = \frac{1}{A_o} \cdot \frac{dw}{dt} \left(2 \pi KT/m \right)^{1/2} \qquad \ldots[15]$$

Though a large number of thermodynamic data at high temperatures has been obtained by this method, many of its aspects viz: the correction to be applied to the shape of the crucible and the effusion hole, the effect of the location of the evaporating surface, the distribution of molecular velocities in the beam and the upper pressure limit at which the method is suitable, are not clear. These problems have been discussed in detail in the literature[31, 37-40]. Apart from the above points, the method has only a limited scope for the study of equilibrium pressures of a reaction involving corrosive species because of the following reasons:

(A) Any reaction of the species with the cell material changes the size of the hole.

(B) The transporting agent has to be separately vaporized and the control of such a pressure is often difficult in the cell.

2.3.5. The Torsion effusion method

In this method the sample is placed in an effusion cell suspended by a fiber. The cell contains two holes in the opposite sides displaced in opposite directions from the centre. The vapour effusion through the holes causes a torque on the cell and the rotational displacement of the cell is measured by a mirror attached to the suspension. This method has received a good deal of attention because of the speed with which the vapour pressure can be obtained and its use for the direct determination of the molecular weight of the effusing species. Searcy and Freeman[40,41] have obtained low values for tin and germanium when compared to the mass spectrometric results. The scope of this method and the limitations are discussed in detail by Gilles[31].

2.3.6. Molecular flow effusion

The molecular flow effusion method has been developed and worked during recent years by DeMarcus[42], Whitman(1953)[43], Modzfeldt(1955)[44], Balson(1961)[45], Farber(1962-66)[46]. This method involves an impinging gas at the temperature of the reaction striking the reacting material at pressures allowing molecular flow. The concentration of the molecular constituents is determined by the equilibrium constant, employing the Knudsen equation:

$$n = P/(2\pi mkt)^{1/2} \qquad \ldots[16]$$

n = number of moles striking the surface.

2.3.7. Optical spectroscopy

None of the experimental methods described above enables to determine the structure and thermodynamic properties of the gases produced in vaporization reactions. Optical spectroscopy can be used for the determination of molecular configuration and electronic, vibrational and rotational energy levels. Thus spectroscopy provides data for the thermodynamic properties by statistical mechanical methods. Emission spectra give information on excited energy levels while absorption spectra are helpful in the characterization of the ground and low energy states. Data on infra red and microwave spectra are useful in determining the structure of diatomic molecules. Details of infra red and microwave spectroscopy are given by Porter, Hughes Klemperrer and Townes et.al.[35] However, this method has limited scope in finding out correct dissociation energies of some compounds. For example, the dissociation energy of NiCl(g) was found to vary 5 ± 2 ev.[47] and 7.3 ev.[48]. This is because the ground state and the electronic energy levels are not clear. The fine structure of NiCl molecule has been determined by Rao, et.al.[49] by the study of its infra red spectrum. ~~They have reported a value of [illegible] ev. For the dissociation energy of NiCl(g).~~

2.3.8. Mass spectrometer

Mass spectrometer is one of the most important tools employed in the high temperature chemistry. The method consists of ionization of the high temperature vapour by electrons and identification of the resulting ions. Inghram and Drowart[50] have given an excellent review on mass spectrometry and its applications to high temperature chemistry.

2.4. FLOW TRANSPIRATION OR TRANSPORTATION METHOD

The transpiration method also known as transportation or entrainment method is one of the oldest and most versatile technique of studying heterogeneous equilibria involving gases and solids. Thomson[51] credits the French chemist Regnault[52] being the first to use this method in 1845. It is used primarily for measuring vapour and dissociation pressures, but it may be applied to gas-solid or gas-liquid equilibria in general. It is one of the few methods that can be used to measure the pressure of a vapour in the presence of large concentrations of other gases.

Excellent reviews by Kubaschewski and Evans[53], Margrave[35], Richardson and Alcock[54] and Schäfer[3] are available in the literature giving applications of the method and the descriptions of many experimental techniques employed in this field. This method deals with the measurement of transport of the material under study. The transport of a substance may be due to appreciable vaporization of the sample at that temperature or may be due to a gas, inert or reactive being passed over a condensed sample at a rate sufficiently low for equilibrium conditions to be established. The gas is collected at some point down stream from the sample and is analysed to determine the vapour and dissociation pressures of components in the sample.

In the vapour-condensed phase equilibria, the solid and liquid which will have no appreciable vapour pressure at that temperature can be transported by the formation of gaseous products of the reaction. In the following case the transport medium is the vapour B

$$a\,A\,(S \text{ or } l) + b\,B(g) = c\,C(g) \qquad \ldots[17]$$

Thus the transport of solid substance presupposes the motion of a gas. In the above reaction if the transport medium has sufficient saturation pressure only at elevated temperatures, then it is added to an inert carrier gas in a heated saturator or is vaporized at the beginning of the system. B(g) is then passed over solid A, transports it and at the end of the system is condensed by cooling. If the reaction proceeds rather extensively and rapidly with the deposition of solid substance one makes use of very simple flow techniques. In the case of this flow technique all the gaseous components migrate with the same speed and hence their ratios are easily known. The gases are assumed ideal and the carrier gas must be saturated with the vapour of the material under study or the products of the reaction.

By Dalton's law the partial pressure of each component p_i is proportional to the number of moles of the gas n_i. Thus for an inert gas flow 'f' and vapour species

$$\frac{p}{p_T} = \frac{p}{p + p_f} = \frac{n}{n + n_f} \qquad \ldots[18]$$

where n can be determined from the loss of weight of a sample from the amount of solid deposited on the cold finger or by the analysis of the products trapped in a flow system. If the molecular weight of the vapour species is known or assumed, n_f known from the flow rate calibration experiments, p_T the pressure at which the system is in equilibrium, p can be determined.

2.4.1. Importance of equilibrium in transport study

The success of the flow method depends on the attainment of equilibrium. In this connection, the following points are to be considered:

1) All the reagents participating in the reaction must be at the equilibrium temperature. This will be facilitated by preheating the gases before they enter the reaction zone. In the case of vapour-liquid or vapour solid equilibria the transport medium with or without diluent gas must be preheated upto the equilibrium temperature before it reacts with solid or liquid and equilibrates with it.

2) The pressure of the equilibrium zone must be the same as that of the entire flow system. Temperature and pressure gradient cause the reverse reaction to occur i.e. the reformation of solid reactants. The apparatus should be so chosen as to avoid these difficulties.

3) The reaction zone must attain equilibrium and remain undisturbed during the transport period. Change of flow rates or very high thermal gradients cause the reaction to shift in such a way that the transport of material observed will differ largely from that of the normal experiments.

4) Some unwanted reactions due to imperfect flow may decrease the surface area of solid, gas or liquid under study, so that the reaction rate will deviate far from equilibrium e.g. in the case of Ni-$NiCl_2$ system, if the carrier gas contains appreciable amounts of O_2, air, water vapour, they will react with Ni or $NiCl_2$ with the formation of oxides thus hindering the reaction giving much lower transport of nickel. The carrier gas therefore has to be perfectly pure and dry.

5) The activity of solid or liquid phase must remain constant throughout the reaction.

6) Flow rate should be measured accurately.

7) Side reactions between sample and container or flow gas or product with the reaction tube should be avoided. Very

few refractory materials are useful for molten metals. For equilibrium measurements, it is therefore necessary to test the materials for which the free energy change for a simpler reduction by the liquid metal has a large positive value. Brewer has illustrated the use of thermodynamics in the search of a suitable container for melting titanium.[55] If an extensive contamination or reaction occurs the materials should be brought to equilibrium with liquid metal or reactive species, so that it is saturated with respect to the solution, either of the metal itself or of the products of the reaction between metal and refractory material. This will minimize the attack or the container will be passivated. Attack by melt normally involves the penetration through a solid container by inter-granular solution process and the rate of this attack depends primarily on kinetic factors e.g. diffusion and viscosity.

2.4.2. Saturation of a carrier gas

The flow or carrier gas should be saturated with vapour. The establishment of the saturation flow is the most important factor in achieving equilibrium. The equilibrium flow rate is different for every system and also dependent on the construction of the apparatus. The flow gas has to ensure equilibrium with solid or liquid. According to Schäfer for this a space where the gas can stay for a fairly long time must be provided. In the simplest case the solid substance is placed in a small vessel which in turn is placed inside a tube of 10 mm. diameter for example. It is better to have the substance in a granular form, packed loosely in the tube over a distance of a few centimeters. The gas passes over the solid in an ideal case equilibrates with it completely. For the above mentioned tube diameter and for the temperature of the solid above 500°C, gas flows from 2-10 liters per hour (20°C, 1 atm.) have usually proved to be satisfactory. When the reaction between gas phase or solid substance proceeds very slowly or when one is forced to use slow gas flow rates, large amounts of solid and long reaction zones are recommended.

The high flow rates can be used if the chemical reaction attains equilibrium quite rapidly. In the high temperature system in which equilibrium is not rapidly attained, diffusion rather than a chemical reaction is usually the rate determining step. Such diffusion processes require longer temperature zones,larger surface area of the sample and slow flow rates. If the flow rate is too high the carrier gas will not be saturated and the apparent pressures will be low. In some cases the heterogeneous reaction proceeds so rapidly that equilibrium will be established at the solid material and the gas motion becomes the slowest step. The majority of the substances have velocity coefficients which are close to 1, i.e.

the surfaces behave as if they are covered with saturated vapour. The quantity of vapour is a function of the saturation pressure and gas kinetics. Consequently a low velocity coefficient will be observed in the transportation from solid to gaseous state. If the carrier gas velocity is too low, sample may be transported due to self diffusion and thermal diffusion. It is, therefore, essential to establish the saturation flow rates where the vapour pressure is independent of flow rate.

If an unsaturated flow gas is suspected a series of experiments at various flow rates should be carried out until a range of flow rate is found for which the mass of sample transported per unit volume of flow gas remains constant. Thus a plot of n_ν/n_o vs n_f (equation 18) should approach a plateau region for n_f values where saturation is complete. For unsaturated flow this plot will not level off. This has been discussed by Lapore and Van Wazer[56]. It has also been customary to make measurements at several flow rates and to extrapolate to zero flow rate to eliminate effect of lack of saturation. If an equilibrium between gaseous phase and a condensed phase is established with negligible diffusion effects the amount of vapour transported per unit time varies with the flow rate of gas mixture[57]. However, it can be shown that at sufficiently high flow rates, diffusion effects become negligible. Diffusion occurs when rate of flow is too slow and the apparent pressures will be too high. Merten[57,29] has derived the equation:

$$p = \frac{m}{tv} \frac{RT}{M} \left[1 - \exp - \left(\frac{v\,l}{DA} \right) \right] \qquad \ldots [19]$$

in which p is the pressure, R, T and M are gas-constant, temperature °K and molecular weight of the species respectively. m/t is the mass transported per unit time, 'l' is the length of the capillary, 'D' is the diffusion coefficient of the vapour and 'A' is the cross sectional area of the capillary. For large values of v (the volume of flow gas) the diffusion effects are important and the pressure assumes the normal value

$$p = (m/t.v)\ (RT/M) \qquad \ldots [20]$$

He has also pointed out that the equation may be used to obtain not only the pressure but also diffusion coefficient in favourable cases. Ackerman <u>et.al.</u>[58] have confirmed the validity of this equation. According to Merten[57] reliable pressure can be calculated if experimental determinations are available at too significantly different flow rates for which saturation has been reached.

2.4.3. Advantages of transportation method

The significance of this technique is brought out in the case of silicon transport in the chloride system[59-61].

Schäfer[59] by using flow method has transported considerable amount of $SiCl_2$ to a cold zone without disproportionation; at lower temperatures it has reacted with $SiCl_4$ to form Si_2Cl_6, Si_3Cl_8, etc.[61]. Another important feature of this method is the ease with which corrosive, unstable vapour species are handled successfully and in a useful way, viz: transport of Al by the monochloride[62].

2.4.4. Disadvantages of the transpiration method

A) The number of molecules vaporizing cannot be known unless the molecular weight of the vapour is known.

B) The difficult situation in this technique is to follow individual species in a heterogeneous system where the products of reaction are more than one gaseous species. Thus the study of reaction involved in the overall process becomes difficult. But the arrangements leading to quantitative collection of the products, condensing on the cold finger, quenching methods and improved analytical techniques may help to solve the problem.

2.5. THERMODYNAMICS AS APPLIED TO EQUILIBRIUM REACTIONS BY TRANSPIRATION

Determination of the vapour pressures of the various components in flow method in solid gas reaction

The amount of solid substance transported by a gas stream in a definite time can be known by knowing the loss in weight of the sample or gain in weight due to the disproportionated solid in a cold trap. The amount of transporting agent passed, and the volume of carrier gas passed can also be known. Then by assuming that the ideal gas law holds good in the equilibrium zone, the pressures can be estimated using the equation:

$$P = \frac{nRT}{V_T} \qquad \ldots[21]$$

Since V_T is related to the initial flow gas V_r, at room temperature T_r the equation becomes

$$P = \frac{nRT_r}{V_r} \qquad \ldots[22]$$

The pressures of various components in a reaction e.g. equation 14, can thus be calculated as follows:

$$P_C = \frac{c}{a}\ \frac{n_A\ RT_r}{V_r} \quad \text{OR} \quad \frac{c}{a}\ \frac{\Delta W\ RT_r}{M\ V_r} \qquad \ldots[23]$$

$$P_B \text{ unreacted} = \left(n_B - \frac{b}{a}\ n_A\right)\frac{RT_r}{V_r} \qquad \ldots[24]$$

OR

$$= \left(n_B - \frac{b}{a}\ \frac{\Delta W}{M}\right)\frac{RT_r}{V_r}$$

The equilibrium constant $K = \dfrac{P_C^c}{P_B^b}$ ...[25]

2.5.1. The equilibrium constant

The state of equilibrium of any process occuring at constant temperature and pressure can be defined by the equation

$$F = 0 \qquad \ldots[26]$$

i.e. that the free energy remains unchanged in any infenitesimal process occuring at constant temperature and pressure. Therefore, in a case of chemical equilibrium, it is important to acquire the information regarding the free energy change in the reaction. Thus for an equilibrium reaction of the type (I) the:

$$\Delta F^{o} = - RT \ln K \qquad \ldots[27]$$

2.6. TREATMENT OF THE EQUILIBRIUM DATA

Experimental equilibrium data determined have been utilized to obtain standard enthalpy of reaction. Two methods have been used, one called the 'Second Law Method' and the other 'The Third Law Method'.

2.6.1. Second Law Method

This involves the utilization of the well known Vant Hoff's equation with the usual log K vs 1/T plot. From the slope of the plot and the intercept one can calculate the heat and entropy of the process respectively. The fundamental basis for this plot lies in the change of standard-free energy with temperature

$$d\left(\frac{\Delta F^{o}}{T}\right) = \frac{\Delta H^{o}}{T^{2}}\ dT = \Delta H^{o} d\left(\frac{1}{T}\right) \qquad \ldots[28]$$

Substituting equation (27) for F^{o} in equation 28, one obtains the Vant Hoff's equation:

$$\frac{d \ln K}{dT} = \frac{\Delta H^{o}}{RT^{2}} \qquad \ldots[29]$$

OR

$$\frac{d(R \ln K)}{d\left(\frac{1}{T}\right)} = \frac{4.5758\ d \log K}{d\left(\frac{1}{T}\right)} = -\Delta H^{o} \qquad \ldots$$

This method is especially useful in numerous cases where the only information available regarding the heat of reaction is derived from the equilibrium measurements.

In the above, it is assumed that ΔC_p^{o} for the process is constant over the temperature range investigated. From Kirchoff's equation

$$\left[\frac{\partial\,(\Delta H^{o})}{\partial\, T}\right]_P = \Delta C_p^{o} \qquad \ldots[30]$$

Therefore, if the heat capacity equations are available for the reactants and products an improved procedure is possible[63,64]. The treatment includes the use of the following equations:

$$\frac{\Delta F}{T} = - R \ln K = \frac{\Delta H^o}{T} - a\ln T - \frac{1}{2} bT - \frac{1}{2} cT^{-2} + I \qquad ...[31]$$

where I is constant.

$$\frac{\Delta H^o}{T} + I = \sum = - R \ln K + \Delta a \ln T + \frac{1}{2} \Delta bT + \frac{1}{2} \Delta cT^{-2} \qquad ...[32]$$

For each temperature at which a value of K is known the right hand side of the above equation can be obtained. As the left hand side of the equation is a linear function of 1/T a plot of $\sum$ against 1/T gives a straight line with a slope ΔH_I^o. From the value of H_I^o one can obtain ΔH_T^o at any temperature range for which the heat capacity equations are applicable.

If the contribution of ΔC_p^o for the reaction is not constant over the temperature range the resultant log K vs 1/T plot will show a curvature or wide scattering of points. In such cases the $\sum$ plot a more satisfactory method than log K vs 1/T is recommended, because it is easier to get the slope of a straight line than that of a curved line.

2.6.2. Third Law Method

This method as its name implies, is fundamentally related to the third law of thermodynamics through its use of absolute entropies and heat capacities. In practice, the free energy function $\frac{F_T^o - H_{T\,ref.}^o}{T}$ also referred as 'fef' is used whenever it is found in a tabulated form or can be calculated. The simplicity and usefulness of these free energy and heat content functions, especially in calculating the heat of reaction were demonstrated by Margrave[65].

The free energy function is related to the usual thermodynamic quantities in the following manner. By rearranging the fundamental free energy equation

$$\Delta F_T^o = \Delta H_T^o - T\,\Delta S_T^o \qquad \ldots[33]$$

one obtains

$$\frac{F_T^o - H_T^o}{T} = -S_T^o \qquad \ldots[34]$$

by adding the quantity $\frac{(H_T^o - H_{T\,ref}^o)}{T}$ (the heat content above a reference temperature usually 0^oK or 298^oK, divided by T) to both sides of the equation one gets

$$\frac{F_T^o - H_{T_{ref}}^o}{T} = -\,S_T^o + \frac{H_T^o - H_{T_{ref}}^o}{T} \qquad \ldots[35]$$

The reference temperature can be converted according to convenience by the use of following relation:

$$\frac{F_T^o - H_{298}^o}{T} = \frac{F_T^o - H_o^o}{T} - \frac{H_{298}^o - H_o^o}{T} \qquad \ldots[36]$$

Since heat content differences and the entropy are related to the C_p values, the free energy function can be evaluated from experimental heat capacity measurements:

$$S_T^o = \int_{T_o}^{T_1} C_p \, d\ln T + \frac{\Delta H_{Tr}}{T_1} + \int_{T_1}^{T_2} C_p \, d\ln T + \quad + \int_{T_1}^{T} C_p d\ln T \qquad \ldots[37]$$

<u>and</u>

$$\frac{H_T^o - H_{T\ ref}^o}{T} = \frac{1}{T} \left(\int_{T_{ref}}^{T_1} C_p dT + \Delta H_{Tr} + \int_{T_1}^{T_2} C_p dT + \quad + \int_{T_1}^{T} C_p dT \right. \qquad \ldots[38]$$

In the case of gaseous molecules it is possible to determine the value of "fef" directly through the use of statistical thermodynamics and spectroscopic data[66].

For a chemical reaction "fef" at a given temperature may be defined as:

$$\Delta fef = (fef)_{products} - ('fef')_{reactants} \qquad \ldots[39]$$

After collection of the terms and consolidation one obtains:

$$\Delta fef = \frac{\Delta F_T^o}{T} - \frac{\Delta H_{T\ ref}^o}{T} \qquad \ldots[40]$$

$$\Delta H_{T\ ref}^o = T\left[\frac{\Delta F_T^o}{T} - \Delta\left(\frac{F_T^o - H_{T\ ref}^o}{T}\right)\right] \qquad \ldots[41]$$

Substituting equation ~~25~~ 27 in equation ~~39,~~ 41 the equation can be written as:

$$\Delta H^{o}_{T_{ref}} = T\,(-R \ln K - \Delta\,'fef') \qquad ...[42]$$

The advantage of the third law method is that each experimentally determined value of the equilibrium constant permits an independent evaluation of the heat of reaction. The free energy functions ~~vary~~ vary very slowly with temperature and hence may be obtained easily and accurately by simple inter and extrapolation procedures from values given at wide intervals. Furthermore, temperature dependent errors are often hard to eliminate from equilibrium measurements. The temperature coefficient and the corresponding heat of reaction from the second law, may be greatly in error whereas the third law heat does not change significantly.

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CHAPTER - 3

SUBLIMATION PRESSURES OF NICKEL DICHLORIDE AND THE EQUILIBRIUM STUDY OF THE REACTION $Ni(c) + NiCl_2(g) = 2NiCl(g)$

CHAPTER - 3

SUBLIMATION PRESSURES OF NICKEL DICHLORIDE AND THE EQUILIBRIUM STUDY OF THE REACTION Ni(c) + $NiCl_2$(g) = 2NiCl(g)

3.1. INTRODUCTION

In the course of his studies on the reaction of anhydrous gaseous chlorides with the corresponding metals Lee[67] has not observed any reaction between nickel chloride gas and nickel metal at 1010°C. However, the lower oxidation state of nickel (viz. NiCl) has been reported. Johnson and Cubiciotti[68] have reported the monovalent nickel in molten state. They have based their evidence on the depression in the freezing point

$$Ni^{o} + Ni^{2} = 2Ni \qquad \ldots[43]$$

McKinley[69] has observed the formation of gaseous nickel monochloride during the kinetic studies on the reaction of chlorine with nickel metal between 1200° and 1700°K. The studies of the band spectra by Mesnage[70], More[71], Müller[72], Krishnamurthy[73], Rao and Reddy[74], have revealed the existence of gaseous nickel monochloride. Schäfer and Etzel[75] have studied the transport of metallic nickel by the reaction

$$Ni(c) + 2HCl(g) = NiCl_2(g) + H_2(g) \qquad \ldots[44]$$

$$Ni(c) + NiCl_2(g) = 2NiCl(g) \qquad \ldots[1]$$

and concluded that hydrogen compounds are necessary for the reaction. A value of 40 ± 92 Kcal./mole for the heat of reaction ΔH_{1300} is reported by them. The data included in Table I show that there is little agreement among the values of heats of formation of NiCl(g) reported. It may be noted that the only experimental value by the transport reaction is reported by Schäfer and Etzel[75].

In view of these discrepancies the study of the equilibrium reaction of $NiCl_2$(g) with Ni(c) at high temperatures has been undertaken. The investigation is carried out employing the well-known transpiration technique.

Before carrying out the equilibrium study of the metal-metal halide reaction, it is necessary to understand the sublimation behaviour of nickel dichloride.

TABLE - I

LITERATURE VALUES FOR THE HEAT OF FORMATION OF NiCl(g)

ΔH_f in Kcals. mole	Method	Author	Reference
15 ± 46	Band Spectra	Gaydon	47
-37.00	Band Spectra	Herzberg	48
>45.0	Chemical transport	Schäfer and Etzel	75
15.0	Calculated	Rossini	76
55.0	Calculated from electronegativities	Allen	77
42.0	Calculated from half dissociation of $NiCl_2(g)$	Schäfer *et.al.*	78
13 24	Calculated	Barber	79
Less than 38.1	Knudsen studies of the sublimation of $NiCl_2$	McCreary and Thorn	81
42.0 ± 5	Flame photometry	Bulzwic	80

SECTION - I

SUBLIMATION OF NICKEL DICHLORIDE

3.1.1. INTRODUCTION

The vapour pressure measurement of nickel dichloride has been studied both by static and flow methods. Employing the static method using nitrogen as the buffer gas, Maier[82] has studied the vapour pressures of a number of metal dichlorides. Schäfer **et.al.**[83] later ~~has~~ have carried out investigations on the vaporization phenomena of the dichlorides of manganese, cobalt, iron, chromium and nickel using the transpiration method. In their studies they have shown that different carrier gases (viz. N_2, A, HCl) have little or no effect on the vapor pressures except when chlorine is used at temperatures more than 800°C. Above 800°C, in the case of chlorine as a carrier gas, the saturation pressures have differed[84] from those below 800°C. The little difference is attributed to the gaseous nickel trichloride, but the existence of which is doubted. Kubaschewski[85, 86] has determined the vapour pressure of nickel chloride.

The vaporization of a number of metal dichlorides employing the mass spectrometer has been studied by Schoonmaker[87] ~~et.al.~~ They have attributed the irregularities in the vapour pressures observed to the existence of the corresponding dimer according to

$$2Mx_2(g) \quad = \quad M_2X_4(g) \qquad \ldots[45]$$

No such dimer is observed by them in the case of nickel dichloride at those temperatures. In a more recent study by McKinley[69] of the reaction between Ni and Cl_2 employing mass spectrometry no dimer for $NiCl_2$ is observed. The only species observed below 1100°K is $NiCl_2$ and at higher temperatures the decrease in the $NiCl_2^+/NiCl^+$ is attributed to the presence of NiCl in the product beam. $NiCl_2$ therefore sublimes predominently as a monomer.

3.1.2. EXPERIMENTAL

(A) Materials

(1) Nickel dichloride - Nickel dichloride hexahydrate (AR quality) was purified to free it from cobalt by the method described by Calabaugh *et.al.*[88]. This consisted of the repeated precipitation of the dihydrate by passing hydrogen chloride gas through a mixture of acetone and a saturated solution of nickel chloride in water. The nickel chloride dihydrate thus obtained was dehydrated by heating at 400°C in presence of HCl gas and flushing out the HCl finally with nitrogen gas for about an hour. The amorphous material obtained was heated under reduced pressure

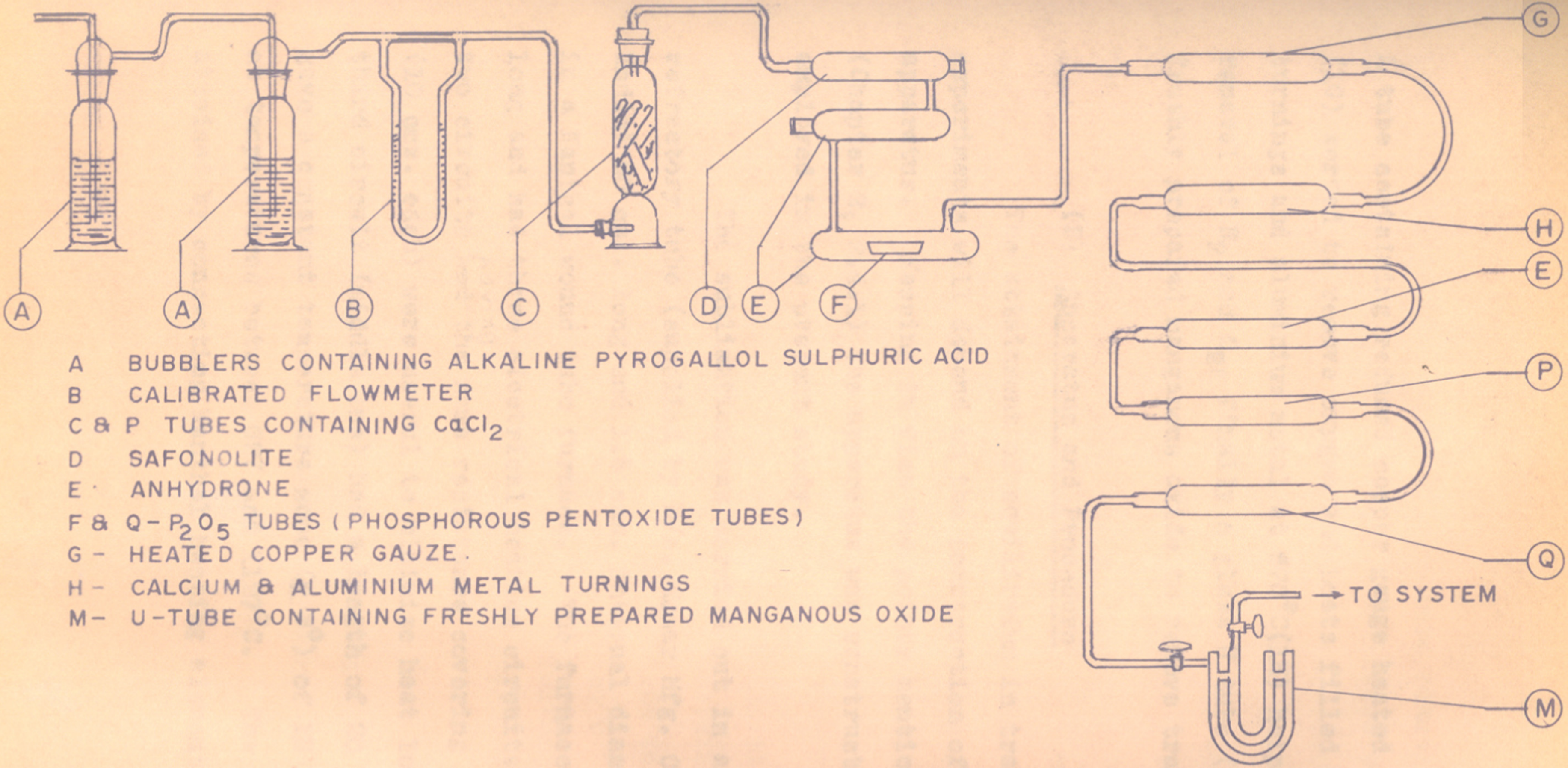
(1 to 2 mm. of Hg) between 700 and 800°C. Golden yellow crystals of pure anhydrous nickel dichloride sublimed off on the colder parts of the system. These showed no traces of cobalt on spectrographic analysis. The dichloride crystals were chemically analysed for chlorine and nickel[89] by standard methods of analysis.[89] The purity was found to be more than 99.9%. The anhydrous crystals were preserved in sealed pyrex glass tubes.

(2) **Argon** - Argon was used as a carrier gas. The gas in cylinder contains impurities like oxygen, moisture and carbon dioxide which affect the main reaction according to the equations:

$$NiCl_2 + H_2O = NiO(c) + 2HCl(g) \qquad ...[46]$$

$$2NiCl_2 + O_2 = 2NiO(c) + 2Cl_2(g) \qquad ...[47]$$

It was, therefore, necessary to remove the impurities from the argon gas by passing it through a purification train schematically shown in Fig. 1. The train consisted of bubbler (1A) containing alkaline pyrogallol and sulphuric acid respectively, a calibrated flow meter (1B) to regulate the gas, two feet long horizontal columns (1D) containing sofonolite to remove CO_2 and tubes containing $CaCl_2$(1C, 1P), anhydrone (1E) and P_2O_5 (1F, 1Q) to remove moisture respectively.



A BUBBLERS CONTAINING ALKALINE PYROGALLOL SULPHURIC ACID
B CALIBRATED FLOWMETER
C & P TUBES CONTAINING $CaCl_2$
D SAFONOLITE
E · ANHYDRONE
F & Q - P_2O_5 TUBES (PHOSPHOROUS PENTOXIDE TUBES)
G - HEATED COPPER GAUZE.
H - CALCIUM & ALUMINIUM METAL TURNINGS
M - U-TUBE CONTAINING FRESHLY PREPARED MANGANOUS OXIDE

FIG. 1. PURIFICATION TRAIN FOR ARGON GAS.

A tube containing reduced copper gauge heated at 600°C (1G) served to remove oxygen and boats filled with calcium turnings and aluminium metal at 670°C(1H) helped the removal of N_2 and O_2, finally a glass U tube (1M) containing freshly prepared manganous oxide to remove traces of oxygen.

(B) Apparatus and Procedure

The attainment of equilibrium in transpiration experiments will depend on the construction of the~~se~~ apparatus. Keeping in view the points mentioned earlier (Chapter 2, 2.4.1) the apparatus was constructed and employed in the present study.

The sublimation was carried out in a mullite refractory tube (supplied by M/s. Kumar Mfg. Co., Calcutta, India) 60 cms. long and 1.5 cms. internal diameter, introduced in a Kanthal wound tube furnace. The furnace was 50 cms. long and had three electrical heating circuits. The outer two circuits ~~had~~ having the same resistance covering the same length (10 cms. each) were useful to minimize heat losses. The third circuit (middle one) had a length of 20 cms. The furnace gave a constant temperature zone (± 3°) of 18 to 20 cms. length at temperatures between 627 and 1127°C. The temperatures were attained by connecting Kanthal heating elements to variable voltage transformers which in turn were connected to a 230V main source through voltage stabilizers to maintain constant power supply. The constant temperature zone was long enough to accommodate an alumina boat of 12 cms. length, 1 cm. in width and 1 cm. in height, leaving 6 to 8 cms. of hot zone for heating the gases. This was useful in bringing all the reactants and carrier gas to the equilibrium temperature. Two cylindrical alumina plugs were placed on either side of the boat. The annular space between the plugs and the tube was sufficiently small so that the plugs served both as radiation shields and as barriers to vapour diffusion.

The insulation around the heating elements consisted of light refractory bricks commercially called "BAGSVIC". These bricks were of advantage in producing less massive and quick heating furnace. These bricks can easily be worked at with mild steel blades or knives. The furnace gave constant temperatures over long periods of time ($\Delta T \pm 3^{o}$ over several hours).

Sections of pyrex glass tubing of suitable sizes were connected to both ends of the reaction tube with a high alumina refractory cement (Accoset-50, supplied by M/s. Associated Cement Company Ltd., India) to give cemented gas tight joints. Through the down stream end a mullite thermocouple sheath entered the reaction tube and was positioned at the centre of the boat. A chromel alumel thermocouple calibrated at various points (viz. at the melting points of zinc, Al and Cu, standard samples of which were procured from the National Bureau of Standards, Washington DC, USA) served to measure the temperature during the experiments. Methods of calibration of thermocouple have been given by Rocser and Wensel[90]. The temperatures were read by measuring the milli-volts at intervals with a thermocouple test set, Cat. No. 7556, W. G. Pye and Co. Ltd., England. Initially the actual boat temperatures were read by inserting the thermocouple in the centre of the boat. Temperatures thus measured were compared with those measured by introducing the thermocouple in the sheath and no difference was observed. A schematic diagram of the transpiration apparatus has been given in Fig. 7.

A calibrated capillary flow meter was employed to measure the flow of argon and arrangements were made to collect the gas during the run. The agreement between the metered and collected quantities of gas was found satisfactory.

In order to know the pressure in the system a by-pass from the out coming gas flow was connected to a U tube mercury manometer and the difference in mercury column was noted in a few experiments. This was about 15 to 20 mm. The total pressure at which the system was in equilibrium was taken as the sum of barometric pressure and the difference in levels of the mercury in the manometer. The average total pressure in all the runs was around 720 mm.

Alumina boat containing nickel dichloride was introduced in the furnace tube after the desired temperature was obtained. Precautions were taken to avoid ~~diluting~~ contaminating the carrier gas with air while inserting and removing the boat in and out of the flow system. The rate of passage of pure argon was brought upto the desired value and the experiment was started. After running the experiment for a definite time (1 hr.) the heating was stopped and the dichloride was pushed out of the hot zone. The boat and the substance were allowed to cool in the argon atmosphere.

In each run the amount of nickel chloride transported was found by weight loss measurements. The dihalide condensed in the colder parts of the tube was carefully collected and weighed. A good agreement between the weight loss and the substance collected was noted within the experimental errors (about 5%).

The rate of transport of nickel chloride as a function of temperature and the rate of flow of argon gas was determined by a series of experiments. The results are given in Table II, Fig. 2.

3.1.2. ATTACK OF $NiCl_2$ ON SILICA TUBE

In a few preliminary experiments using reaction tubes made of silica it was observed that the inside walls of the tube were coated with green coloured product which when scraped and analysed showed the presence of NiO. During these experiments free chlorine was also observed indicating that $NiCl_2$ reacted with silica giving Cl_2 and NiO. In some experiments white fumes were also observed. They were due to the presence of $SiCl_4$ vapors. The following reactions were found to take place with silica tubes:

$$SiO_2(c) + 2NiCl_2(g) = 2NiO(c) + SiCl_4(g) \quad ...[48]$$

$$SiO_2(c) + 2NiCl_2(g) = 2NiO(c) + SiCl_2(g) + Cl_2(g) \quad ...[49]$$

Experiments were therefore carried out in refractory tubes in which the above difficulties were avoided. Silica boats were replaced by those of alumina. The sublimation of $NiCl_2$ was studied at different temperatures and with different carrier gases viz. A, N_2 and HCl.

3.1.4. TREATMENT OF THE DATA

In the study of the sublimation over the temperature range 1030-1116°K the experimental weight loss data of $NiCl_2$ was used to calculate its sublimation pressure. The pressure can be calculated from the equation 22:

$$P = n.RT\overset{r}{\cancel{n}}/Vr \qquad \ldots[22]$$

where P = The pressure.

n = The number of moles of $NiCl_2$ transported.

R = Gas constant.

Vr = Volume of argon in liters at temperatures T_r °K.

3.1.5. EFFECT OF FLOW OF ARGON ON THE SUBLIMATION OF $NiCl_2$

It had become necessary to determine the limits of flow rates of the carrier gas which was saturated with the gaseous halide. This helped to know the extent to which the experimental results were being influenced by diffusion transport. It also helped to know whether the equilibrium between a gas phase and a condensed phase was established or not. With negligible diffusion effect the amount of vapour transported per unit time varied linearly with the flow rate of the gas mixture[57]. The results are tabulated in Table II.

TABLE - II

TRANSPORT OF $NiCl_2$ WITH CHANGE IN FLOW RATE OF THE CARRIER GAS(ARGON) AT 1061°K

Argon passed Liters/hr.	$NiCl_2$ transported in gms.	-Log P
0.52	0.09675	1.4546
0.64	0.10780	1.4979
1.08	0.14890	1.5848
1.52	0.21120	1.5814
2.24	0.31360	1.5782
3.04	0.42555	1.5782
3.82	0.53475	1.5783
4.30	0.59965	1.5799
4.62	0.64880	1.5768
5.02	0.68265	1.5908
5.14	0.70200	1.5890

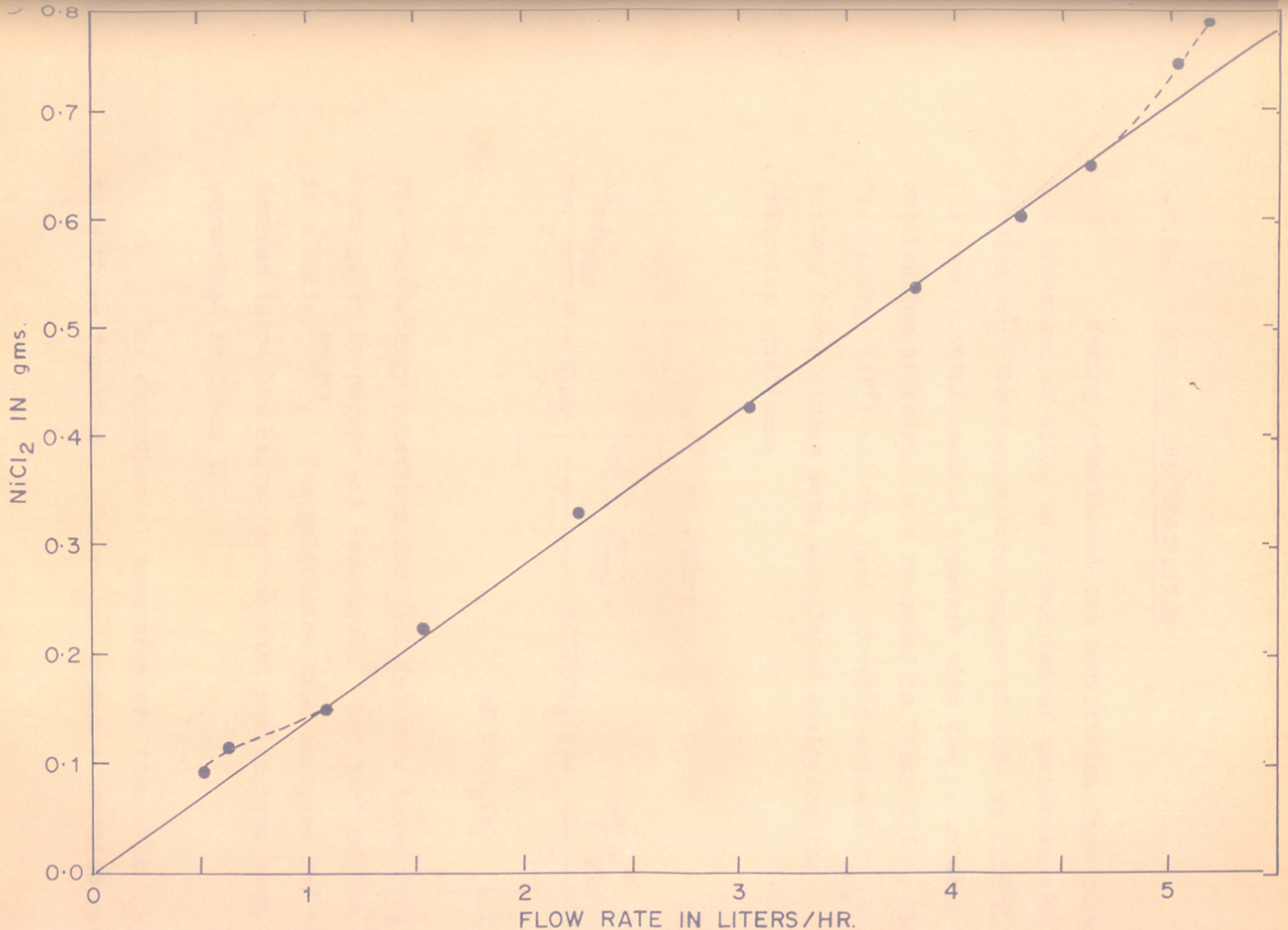


FIG. 2. PLOT OF TRANSPORT OF $NiCl_2$ VS FLOW RATE (ARGON)

3.1.5. RESULTS AND DISCUSSION

Having established the equilibrium flow rate the transport of $NiCl_2$ as a function of temperature was studied ~~over~~ in the temperature region of 1030 to 1116°K. The experimental results together with the calculated sublimation pressures were recorded in Table III. The free energy (ΔF^o) and the heat of sublimation (ΔH_{sub}) at various temperatures were calculated employing the following equations:

$$\Delta F^o = -RT\ln p \qquad \ldots[50]$$

$$\frac{\Delta H^o_{sub_{298}}}{T} = -R\ln p - \left[\frac{\left(F^o_T - H^o_{298}\right)}{T} \text{ of } NiCl_2(g) - \frac{\left(F^o_T - H^o_{298}\right)}{T} \text{ of } NiCl_2(c) \right] \qquad \ldots[51]$$

The free energy functions for $NiCl_2(g)$ were taken from the data given by Brewer and Somayajulu[91] and that of the solid from Kelley[92,93]. The calculated free energies and the derived third law heats for the sublimation have been summarized in Table IV.

The experimental pressures are some what higher than those reported. The vapour pressure equation can be

T A B L E - III

TRANSPIRATION DATA ON THE SUBLIMATION OF $NiCl_2$

Temp. ^{o}K	Flow rate(ΔV) liters/hour	ΔW in grams of $NiCl_2$ transported	$n = NiCl_2$ transported in moles	$p = n.\frac{RT}{\Delta V}$ atmos.
1030	1.20	0.07960	6.13913×10^{-4}	1.2509×10^{-2}
1041	1.48	0.14050	1.08360×10^{-3}	1.7903×10^{-2}
1048	1.43	0.15025	1.15880×10^{-3}	1.9815×10^{-2}
1077	2.51	0.50325	3.8813×10^{-3}	3.7811×10^{-2}
1093	1.16	0.35695	2.7529×10^{-3}	5.8031×10^{-2}
1106	2.08	0.70905	5.4685×10^{-3}	6.4287×10^{-2}
1116	1.02	0.5314	4.0984×10^{-3}	9.8249×10^{-2}
1	2	5	3	4

TABLE - IV

THIRD LAW HEATS FOR THE SUBLIMATION OF $NiCl_2$

Temp. °K	-Log p	ΔF_t K.cals.mole^{-1}	$T \Delta fef$ K.cals.mole^{-1}	$\Delta H_{sub\ 298}$ K.cal. mole^{-1}	$\Delta H_{sub\ 298}$ K.cal.mole^{-1}
1030	1.9031	8.9694	49.4090	58.3784	58.38
1041	1.7471	8.3222	49.9060	58.2282	58.23
1048	1.7031	8.1671	50.2410	58.4081	58.41
1077	1.4244	7.0098	51.5880	58.5978	58.60
1093	1.2364	6.1836	52.3200	58.5036	58.50
1106	1.1919	6.0320	52.9440	58.9764	58.98
1116	1.0077	5.1459	53.4120	58.5579	58.56
	5	6	7		8

Average : 58.52 K.cal. mole^{-1}

Standard deviation : 0.45 K.cal.mole^{-1}

Standard error of mean : 0.17 K.cal.mole^{-1}

$\Delta H_{sub\ 298} = 58.52 \pm 0.45$ K.cals. mole^{-1}

given by:

$$\text{Log P atm.} = -\frac{11{,}2733 \pm 478.6}{T} + 9.0563 \pm 0.446 \qquad \ldots[52]$$

The sublimation temperature derived from this at one atmosphere (760 mm. of Hg) is 1244.8°K.

Employing the well-known Vant Hoff's equation

$$d \ln p/d(1/T) = \frac{-\Delta H_{sub}}{R} \qquad \ldots[53]$$

the heat of sublimation was determined from the plot of the logarithm of the sublimation pressure versus the reciprocal of the absolute temperature (Fig.3). The constants from equation 53 led to a value of ΔH_{sub} at 1073°K 51.58 ± 2.2 Kcal. mole^{-1}. It represented the mean value over the temperature range studied and did not take into account the effect of C_p. According to Brewer[94] the change in the C_p is -10 cals. deg.$^{-1}$ mole^{-1} when a substance changes from a solid to gas. This difference in the C_p when integrated between the limits 298 and 1073 gives $\Delta(H^o_{1073} - H^o_{298})$

$$\int_{298}^{1073} C_p\,dT = \Delta(H^o_{1073} - H^o_{298}) \qquad \ldots[54]$$

$$\Delta C_p \quad (1073-298) = \Delta(H^o_{1073} - H^o_{298}) \qquad \ldots[55]$$

$$-10(1073-298) = 7.750 \text{ Kcals.} \qquad \ldots[56]$$

This when added to the above value of heat of sublimation at 1073°K yields $\Delta H_{sub_{298}}$ 59.33 ± 2.2 Kcals. mole^{-1}.

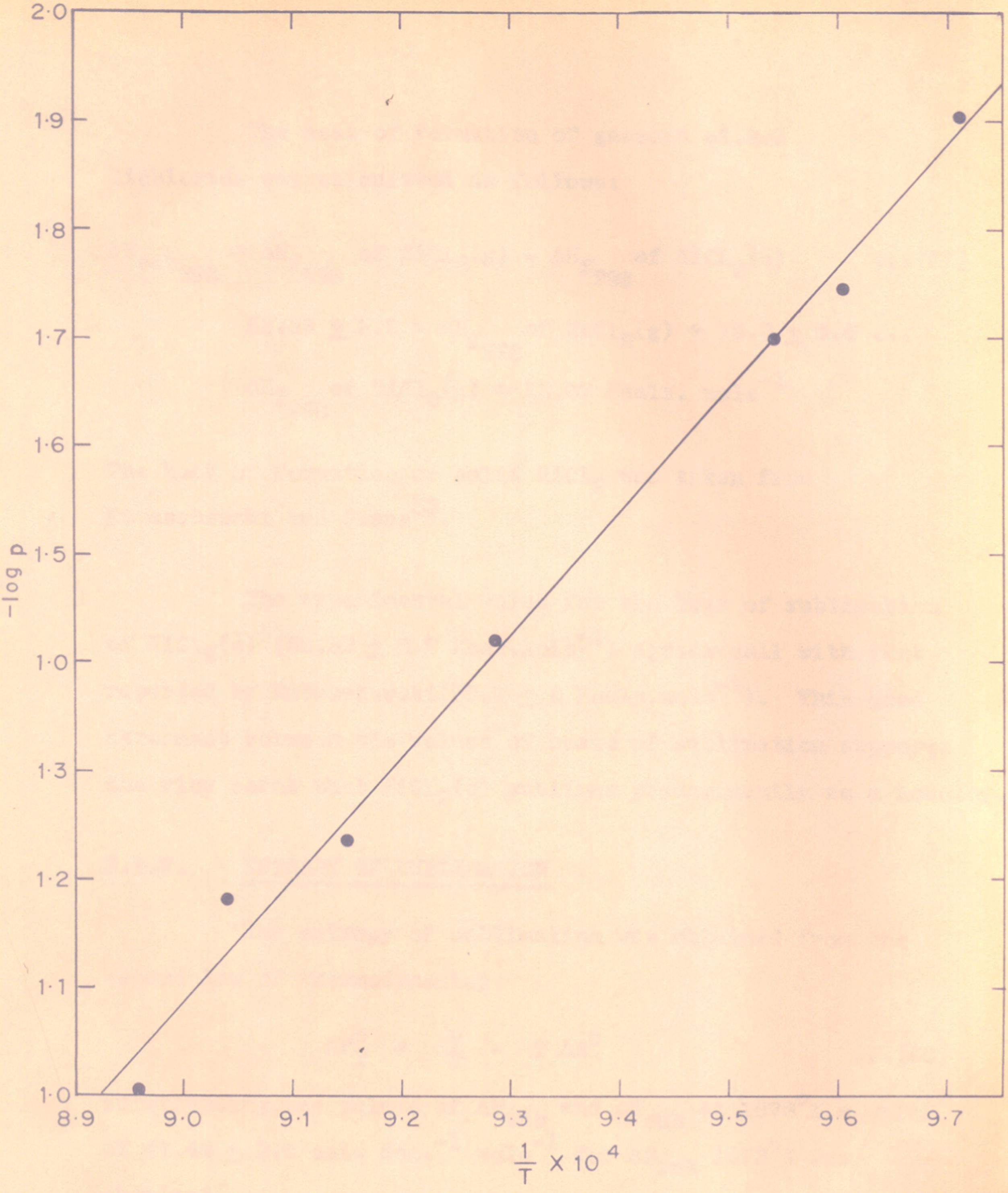


FIG. 3. PLOT OF LOG p VS $\frac{1}{T}$ FOR SUBLIMATION OF $NiCl_2$

The heat of formation of gaseous nickel dichloride was calculated as follows:

$$\Delta H_{sub_{298}} = \Delta H_{f_{298}} \text{ of } NiCl_2(g) - \Delta H_{f_{298}} \text{ of } NiCl_2(c) \qquad \ldots[57]$$

$$59.33 \pm 2.2 = \Delta H_{f_{298}} \text{ of } NiCl_2(g) + 73.0 \pm 0.5 \ldots$$

$$\Delta H_{f_{298}} \text{ of } NiCl_2(g) = -13.67 \text{ Kcals. mole}^{-1}$$

The heat of formation of solid $NiCl_2$ was taken from Kubaschewski and Evans[53].

The experimental value for the heat of sublimation of $NiCl_2(c)$ (59.33 ± 2.2 Kcal.mole^{-1}) agrees well with that reported by Kubaschewski(59.1 ± 2 Kcals.mole^{-1}). This good agreement between the values of heats of sublimation supports the view point that $NiCl_2(c)$ sublimes predominantly as a monomer.

3.1.7. ENTROPY OF SUBLIMATION

The entropy of sublimation was obtained from the second law of thermodynamics:

$$\Delta F^o_T = H^o_T - T\,\Delta S^o \qquad \ldots[58]$$

substituting the values of ΔF_{sub} and ΔH_{sub} at 1073°K a value of 41.44 ± 2.0 cal. deg.$^{-1}$ mole^{-1} for ΔS_{sub} 1073°K was obtained.

SECTION - II

EQUILIBRIUM STUDY OF THE REACTION
$Ni(c) + NiCl_2(g) = 2NiCl(g)$

3.2. INTRODUCTION

The equilibrium reaction between gaseous nickel dichloride and Ni(c) may be understood by considering the following reactions:

$$Ni(c) + NiCl_2(g) = 2NiCl(g) \qquad ...[1]$$

$$NiCl_2(g) = NiCl(g) + 1/2\ Cl_2(g) \qquad ...[59]$$

$$NiCl_2(g) + 1/2\ Cl_2(g) = NiCl_3(g) \qquad ...[60]$$

To study the possibilities of reaction (59) the sublimation pressures were determined but in the course of the experiment no evolution of chlorine was observed and hence the reaction can be rejected. Schäfer and Breil[85] in their work stated that when chlorine was used as carrier gas, small discrepancies in the pressures were observed and concluded that these were due to the formation of gaseous trichloride. In the present work argon was used as a carrier gas and hence reaction (60) can be neglected.

CHAPTER - 4

REACTION OF $AlCl_3(g)$ WITH $NiO(c)$ AT HIGH TEMPERATURES

3.2.1. EXPERIMENTAL

[A] Materials

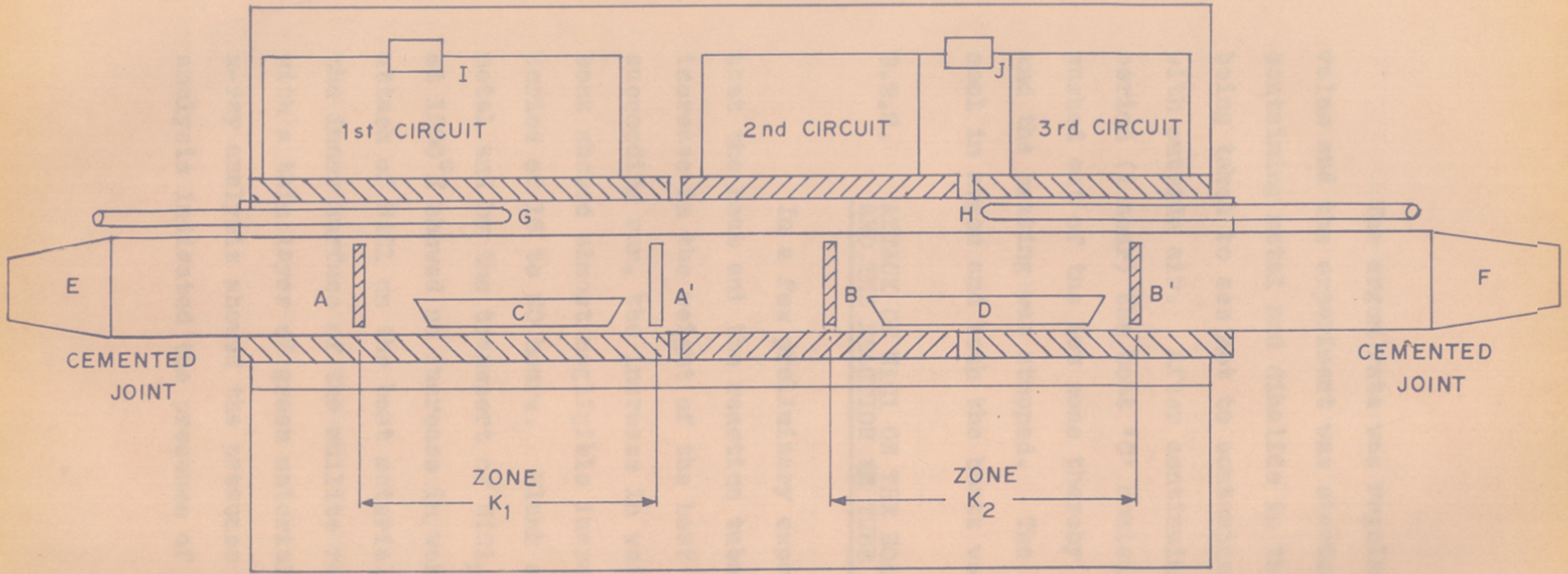
(1) Nickel metal - Spec-pure nickel metal was used throughout the investigations. Its spectrographic analysis revealed traces of silicon.

(2) Nickel dichloride - Purified and resublimed (described earlier) nickel dichloride was used.

(3) Argon - Argon purified by the method described earlier was used as carrier gas.

[B] Apparatus and procedure

An experimental set up shown in Fig.IV was employed for the equilibrium study of the reaction. It consisted of a tube furnace having two constant temperature zones K_1 and K_2 of 15 to 20 cms. long. The zone K_1 was kept constant at about 800°C and the zone K_2 at the reaction temperatures (970-1100°C). The boat 'D' containing nickel metal was introduced in the zone K_2 and the boat with the dihalide in the zone K_1 in the flow of argon after getting the required temperatures. In addition refractory plugs A, A', B, B' of suitable sizes were introduced at the proper points to act as radiation shields and diffusion barriers, without which the equilibrium could not be obtained easily.



A, B
A', B' RADIATION SHIELDS

C, D – BOATS CONTAINING METAL HALIDE AND METAL

E, F – B_{24} MALE GLASS JOINTS

G, H – THERMOCOUPLE SHEATHS

I, J – VARIACS CONNECTED THROUGH VOLTAGE STABILIZER

K_1, K_2 – CONSTANT TEMPERATURE ZONES

FIG. 4. FURNACE FOR THE STUDY OF THE EQUILIBRIUM REACTION $Ni_{(c)} + NiCl_{2\,(g)} = 2NiCl_{(g)}$

The argon rate was regulated to the desired value and the experiment was started by pushing boats containing metal and dihalide in the hot zone. Care being taken to see not to contaminate the carrier gas with outside air. After continuing the run for definite period (1 hour) the boat 'C' containing the dihalide was pushed out of the hot zone thereby arresting the reaction and the heating was stopped. The system was allowed to cool in argon and both the boats were weighed.

3.2.2. ATTACK OF $NiCl$ ON THE BOAT AND THE REACTION TUBE

In a few preliminary experiments it was observed that the boat and the reaction tube were attacked and an increase in the weight of the boat was noticed. After each succeeding run, the increase in weight was reduced. The boat showed almost negligible increase in weight after a total period of 16 to 20 hours. Blank experiments with nickel metal and by the transport of $NiCl_2$ vapour with an empty boat at $1200^{\circ}K$ showed no increase in weight. In addition to the attack of $NiCl$ on the boat material, it was observed that the inner surface of the mullite reaction tube got covered with a thin layer of green material. It was collected and the x-ray analysis showed the presence of NiO. Spectrographic analysis indicated the presence of silicon in addition to NiO.

It was only after the formation of the protective layer of the green material reliable experimental results could be obtained. The reaction was studied as follows:

1) Study of the reaction at constant partial pressure of $NiCl_2$ at one temperature as a function of the rate of flow of carrier gas.

2) Influence of temperature on the reaction.

3.2.3. TREATMENT OF THE DATA

In the study of the equilibrium reaction over the temperature range 1243 - 1396°K, the experimentally determined weight loss data of Ni and $NiCl_2$ were used to calculate the partial pressures of NiCl and $NiCl_2$. The vapour pressure of NiCl formed during the reaction at high temperatures was calculated from:

$$P_{NiCl} = \frac{n_a RTr}{Vr} \qquad \ldots [22]$$

$$P_{NiCl_2} = \frac{n_b RTr}{Vr}$$

The number of moles of NiCl and $NiCl_2$ were calculated as follows from the loss in weight (ΔW) of Ni and $NiCl_2$:

$$n_a = \frac{2 \times \Delta W.Ni}{Mol.wt.Ni} \qquad \ldots [61]$$

$$n_b = \frac{\Delta W\ NiCl_2}{Mol.wt.NiCl_2} \qquad \ldots [62]$$

The equilibrium constant K_p can be calculated from the equation:

$$K_p = \frac{P_a^2}{P_b} \qquad \ldots [63]$$

3.2.4. EFFECT OF FLOW OF ARGON ON THE TRANSPORT OF NICKEL

To know the extent to which the experiments were being influenced by diffusion transport, the limits of the flow gas were studied. This helped to know whether the equilibrium between a condensed phase and a gas phase was established or not. With negligible diffusion effect the transport of nickel varied linearly with the flow of argon. The results are tabulated in Table V. The linear portion in Fig. 5 indicates the flow rates necessary for the equilibrium.

3.2.5. RESULTS AND DISCUSSION

The experimental results obtained in the transpiration study of the equilibrium reaction (1) are tabulated in Table V. The calculated log K_ps and the free energies were also included. The obtained log K_p value~~s~~ are plotted against the reciprocal of the absolute temperatures (Fig.VI). The slope of the plot

TABLE - V

TRANSPORT OF NICKEL METAL WITH CHANGE IN THE FLOW RATE AT 1300°K

Flow rate Litre/hr.	$NiCl_2$ transport moles	NiCl transport in mg.ml.	$K_P \times 10^{-4}$	$-\log K_P$
0.80	1.1555×10^{-3}	3.00	2.8907	3.5389
1.10	1.492×10^{-3}	3.40	2.0820	3.6815
1.90	2.578×10^{-3}	5.75	1.9860	3.7020
2.40	3.255×10^{-3}	7.20	1.9570	3.7089
3.40	4.612×10^{-3}	10.40	2.0340	3.6917
4.20	5.148×10^{-3}	13.00	2.1039	3.6770
4.50	6.102×10^{-3}	13.50	1.9580	3.7082
4.70	1.193×10^{-3}	13.75	1.9154	3.7178

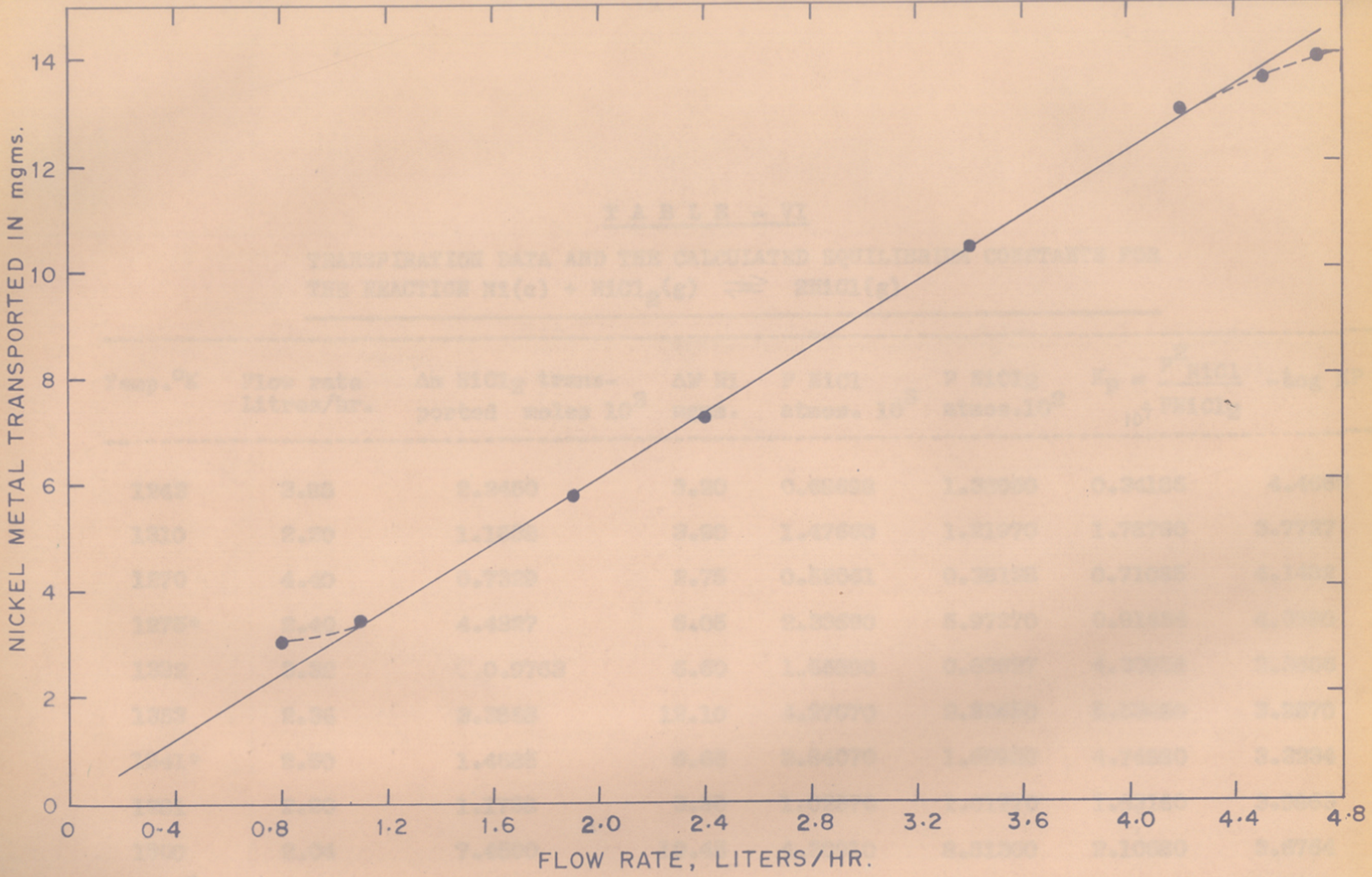


FIG. 5. PLOT OF TRANSPORT OF NICKEL METAL VS FLOWRATE
(ARGON GAS CONTG. $NiCl_2$).

TABLE - VI

TRANSPIRATION DATA AND THE CALCULATED EQUILIBRIUM CONSTANTS FOR THE REACTION $Ni(c) + NiCl_2(g) \rightleftharpoons 2NiCl(g)$

Temp. °K	Flow rate Litres/hr.	Δn $NiCl_2$ transported moles 10^3	ΔW Ni mgms.	P NiCl atmos. 10^3	P $NiCl_2$ atmos. 10^2	$K_p = \frac{P^2_{NiCl}}{P_{NiCl_2}}$ 10^4	-Log KP
1243	3.88	2.2450	3.20	0.68698	1.38050	0.34186	4.4662
1310	2.20	1.1638	3.90	1.47660	1.21970	1.78760	3.7727
1270	4.40	0.7329	2.75	0.52061	0.38128	0.71085	4.1482
1275*	2.40	4.4827	5.05	2.33690	5.97270	0.91434	4.0390
1332	3.32	0.9763	6.60	1.65590	0.63627	4.30950	3.3656
1353	2.36	3.3868	12.10	4.27070	3.29550	5.53450	3.2570
1341*	2.60	1.4685	6.65	2.84070	1.69930	4.74880	3.3234
1281	2.20	1.1738	3.30	1.02570	1.01970	1.03180	3.9863
1300	2.04	7.4590	10.45	4.30910	8.81360	2.10680	3.6764
1398°	2.80	4.6162	28.45	7.7954	3.32320	18.28600	2.7381

* Experiments carried out for 45 minutes.

o Experiments carried out for 65 minutes.

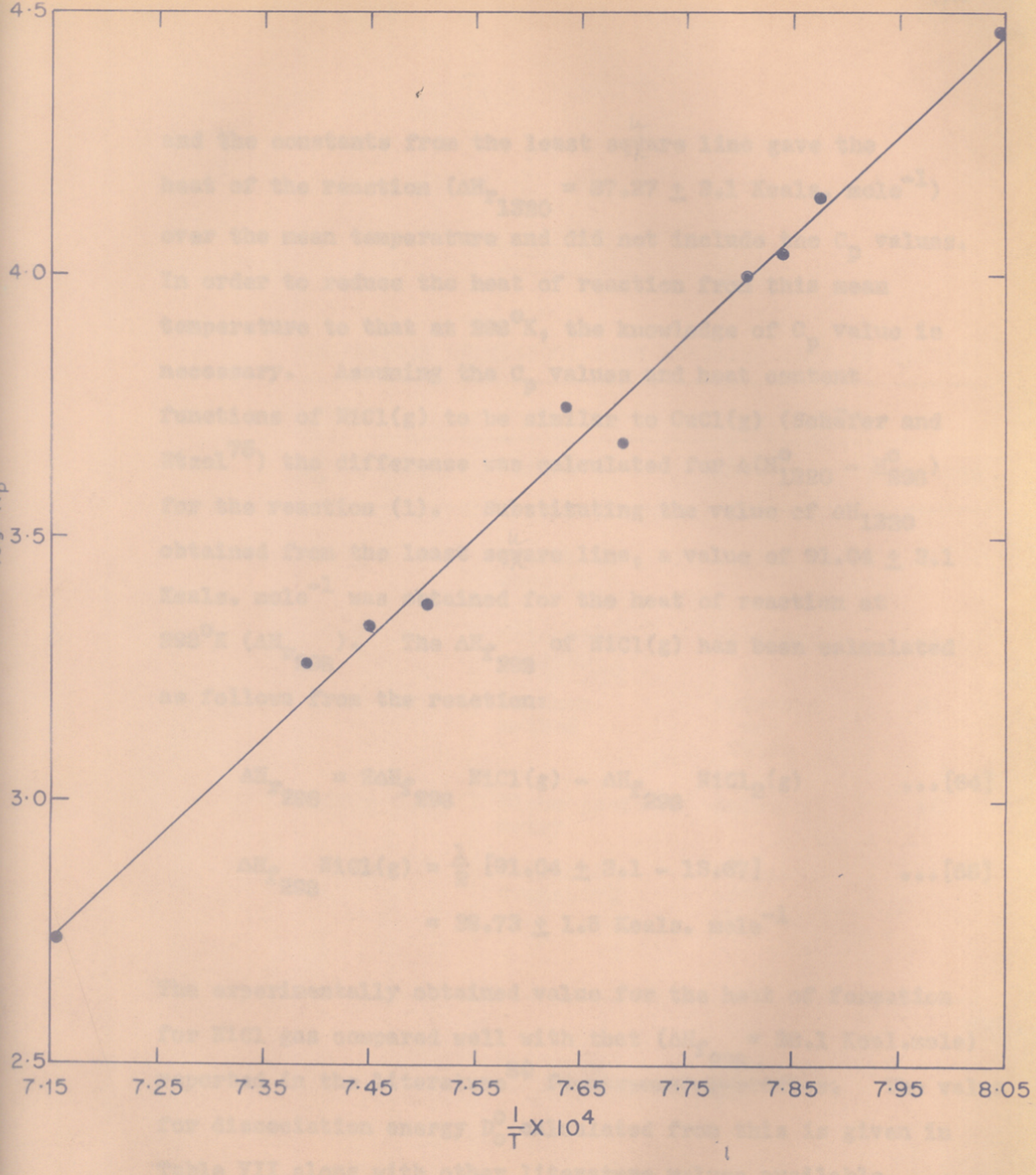


FIG. 6. PLOT OF LOG K_p VS $\frac{1}{T} \times 10^4$ FOR THE REACTION

$Ni_{(c)} + NiCl_{2\,(g)} = 2\,NiCl_{(g)}$

and the constants from the least square line gave the heat of the reaction ($\Delta H_{r_{1320}} = 87.27 \pm 3.1$ Kcals. mole^{-1}) over the mean temperature and did not include the C_p values. In order to reduce the heat of reaction from this mean temperature to that at 298°K, the knowledge of C_p value is necessary. Assuming the C_p values and heat content functions of NiCl(g) to be similar to CuCl(g) (Schäfer and Etzel[75]) the difference was calculated for $\Delta(H^o_{1320} - H^o_{298})$ for the reaction (1). Substituting the value of ΔH_{1320} obtained from the least square line, a value of 91.04 ± 3.1 Kcals. mole^{-1} was obtained for the heat of reaction at 298°K ($\Delta H_{r_{298}}$). The $\Delta H_{f_{298}}$ of NiCl(g) has been calculated as follows from the reaction:

$$\Delta H_{r_{298}} = 2\Delta H_{f_{298}} \text{ NiCl(g)} - \Delta H_{f_{298}} \text{ NiCl}_2\text{(g)} \qquad \ldots[64]$$

$$\Delta H_{f_{298}} \text{NiCl(g)} = \frac{1}{2}\,[91.04 \pm 3.1 - 13.67] \qquad \ldots[65]$$

$$= 38.73 \pm 1.5 \text{ Kcals. mole}^{-1}$$

The experimentally obtained value for the heat of formation for NiCl gas compared well with that ($\Delta H_{f_{298}} = 38.1$ Kcal.mole) reported in the literature[80] ~~from spectral studies~~. The value for dissociation energy D^o_o calculated from this is given in Table VII along with other literature values available.

TABLE - VII

COMPARISON OF DISSOCIATION ENERGIES (D_0^o) OF NiCl(g)

D_0^o in e.v.	Method	Author	Reference
5 ± 2	Molecular spectra	Gaydon	47
7.3	Molecular spectra	Herzberg	48
<4	Knudsen method	McCreary and Thorn	81
3.88 ± 0.2	Flame photometry	Bulzwic	80
3.98	Chemical transport	Present work Chapter III	

3.2.6. ENTROPY OF REACTION

The entropy of reaction was obtained by substituting the values for ΔF°_{1320} and ΔH°_{1320} for the equilibrium reaction (1) in the equqtion (56). A value of 49.85 ± 7.5 cals. $\mathrm{deg.}^{-1}$ mole^{-1} was obtained for the entropy of reaction at 1320°K.

3.2.7. CALCULATION OF ENTROPY OF NiCl(g) AT 1320°K

$$\Delta S_{r_{1320}} = [2\Delta S_{1320}\mathrm{NiCl} - (\Delta S_{1320}\ \mathrm{Ni} - \Delta S_{1320}\ \mathrm{NiCl}_2)] \qquad \ldots[66]$$

$$\Delta S_{1320}\mathrm{NiCl(g)} = 1/2[\Delta S_{r_{1320}} + \Delta S_{1320}\ \mathrm{Ni} + \Delta S_{1320}\ \mathrm{NiCl_2(g)}] \ldots[67]$$

$$= 1/2\ [49.85 + 18.19 + 95.50]$$

$$= 81.78 \pm 3.7 \text{ cals. deg.}^{-1} \text{ mole}^{-1}$$

The value of ΔS_{1320} NiCl(g) compared well with that of the value from NBS (ΔS_{1300} NiCl(g) = 77.2 cals. $\mathrm{deg.}^{-1}$ mole^{-1})[95].

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TABLE - VIII

THERMODYNAMIC DATA FOR THE SUBLIMATION OF $NiCl_2$ AND THE EQUILIBRIUM REACTION:
$Ni(c) + NiCl_2(g) = 2NiCl(g)$

$$\text{Log } P = \frac{-11{,}273.3 \pm 478.6}{T} + 9.0563 \pm 0.446$$

Sublimation temperature = 1244.8°K at 760 mm. of Hg.

ΔH_{sub} at 298°K Second Law = 59.33 ± 2.2 Kcals. $mole^{-1}$.

ΔH_{sub} at 298°K Third Law = 58.62 ± 0.45 Kcals. $mole^{-1}$.

ΔH_f of $NiCl_2(g)$ at 298°K = -13.67 ± 1.1 Kcals. $mole^{-1}$.

ΔH_r at 1320°K = 87.27 ± 3.1 Kcals. $mole^{-1}$.

ΔS_r at 1320°K = 49.85 ± 7.5 cals. $deg.^{-1}$ $mole^{-1}$.

ΔH_r at 298°K = 91.04 ± 3.1 Kcals. $mole^{-1}$.

ΔH_f at 298°K for NiCl(g) = 38.73 ± 1.5 Kcals. $mole^{-1}$.

ΔS_{1320} for NiCl(g) = 81.78 ± 3.7 cals. $deg.^{-1}$ $mole^{-1}$.

CHAPTER - 4

REACTION OF $AlCl_3$(g) WITH NiO(c) AT HIGH TEMPERATURES

4.1. INTRODUCTION

In the literature[3] it has been stated that whenever a metal halide reacts with an oxide of a divalent metal there is the possibility of the formation of the corresponding oxyhalide according to the equation

$$MeO(c) + RX_n(g) = MeX_2(g) + ROX_{n-2}(g) \qquad ...[68]$$

Schäfer *et.al.*[96] have shown the formation of solid AlOCl by the interaction of aluminium chloride with metallic oxides viz. V_2O_5, Nb_2O_5, Ta_2O_5, MoO_3, WO_3, in a sealed tube at 270 to 300°C. Fischer and Gewehr[97] have proposed the formation of aluminium oxychloride in gaseous state as one of the products when alumina reacts with chlorine or hydrogen chloride at 1250°C. The existence of some of the gaseous oxyhalides of light metals like boron and aluminium has been shown by Farber and Blauer[98] and Farber and Petersen[99]. Greenbaum *et.al.*[100] have proved the existence of gaseous

AlOCl at 2400°K and claimed to be the first to determine its heat of formation experimentally using the molecular effusion method in the study of the reaction

$$1/3\ Al_2O_3(l) + 1/3\ AlCl_3(g) = AlOCl(g) \qquad ...[69]$$

Semenkovitch[101] has reported the action of AlCl(g) on refractory oxides viz. MgO, BeO, ZrO_2 and SiO_2 but with Al_2O_3 no reaction has been observed. His experiments are quantitative and the spinel formation has been overlooked in his experiments. Rao and Dadape[14] have studied the equilibrium reaction (70) indicating the spinel formation

$$4MgO(c) + 3AlCl(g) = MgAl_2O_4(c) + AlCl_3(g) + 3Mg(g) \qquad ...[70]$$

When gaseous $AlCl_3$ is passed over nickel oxide at high temperature the reaction taking place can be represented by the following equations

$$NiO(c) + AlCl_3(g) = NiCl_2(g) + AlOCl(g) \qquad ...[71]$$

$$3NiO(c) + 2AlCl_3(g) = 3NiCl_2(g) + Al_2O_3(c) \qquad ...[72]$$

Preliminary experiments have shown an azure coloured product the yield of which gets increased with increase in temperature. The azone product is found to be nickel aluminate spinel on x-ray analysis. The presence of the nickel spinel can be explained by the reaction

$$4NiO(c) + 2AlCl_3(g) = NiAl_2O_4(c) + 3NiCl_2(g) \quad ...[73]$$

Nickel aluminate has been prepared by grinding equimolar quantities of NiO and Al_2O_3 on heating at 1300 to 1400°C for longer hours. Lenov and Novokhartskii[102] have prepared the spinel by grinding an equimolar mixture of AR grade NiO and Al_2O_3, briquetting and sintering it at 1300°C for 26 hours in an atmosphere of CO_2 containing 15% of CO.

As the preliminary experiments have shown the increase of the product with increase in temperatures, it shows that the equilibrium reaction is endothermic and must occur with an increase of entropy according to the principle of successive entropy states. In this connection, Brewer has also stated that a gas will only react endothermically with a solid to produce a significant yield of the reaction product if the reaction produces at least as many moles of gas as are consumed in the reaction. In order to establish the reaction scheme, the equilibrium measurements are carried out together with the identification of the products.

The calculated free energies and log K_ps for reactions of $AlCl_3$ with several metallic oxides are tabulated in Table IX. The change in free energy and the log K_ps with temperature are shown in Fig. IX and X. From the data it can be seen that the reactions of $AlCl_3$ with calcium oxide and nickel oxide are more favourable at these temperatures. It can also be seen that the free energy of the reaction 71 at 2400°K is the same as that of reaction 69 at 1500°K.

4.2. EXPERIMENTAL

(A) Materials

(1) Nickel oxide (NiO) - Black nickel oxide of AR quality was heated at 1400°C for about 8 hours to get the green oxide. The green crystals were analysed chemically by the standard method for nickel. The purity of the product was found to be more than 99.5 per cent. X-ray powder patterns of the solid showed the presence of NiO only ~~(Table~~ X

Spectrographic analysis revealed the presence of traces of cobalt and silicon.

(2) Aluminium trichloride - $AlCl_3$ with 99.9% purity (E. Merck grade) was resublimed in an inert atmosphere before use. The resublimed product contained 0.04% of $FeCl_3$ and 0.02% alumina.

TABLE - X

CALCULATED FREE ENERGIES AND LOG KPS FOR VARIOUS REACTIONS AT DIFFERENT TEMPERATURES

Reaction	ΔF_T K.cals.mole^{-1}			-Log KP				ΔF_T
	500	1000	1500	500	1000	1500	298	298
$Al_2O_3(c) + AlCl_3(g) = 3AlOCl(g)^*$	244.3	199.8	156.8	106.76	43.66	22.85	192.65	262.7
$Al_2O_3(c) + 2HCl(g) = 2AlOCl(g) + H_2O(g)$	131.1	101.4	73.2	53.31	22.16	10.67	105.35	143.6
$Al_2O_3(c) + Cl_2(g) = 2AlOCl(g) + \frac{1}{2}O_2(g)$	194.8	157.1	120.7	85.17	34.33	17.59	154.41	210.6
$CaO(c) + AlCl_3(g) = AlOCl(g) + CaCl_2(g)$	67.0	45.8	25.4	29.32	10.01	3.70	55.67	75.9
$MgO(c) + AlCl_3(g) = AlOCl(g) + MgCl_2(g)$	77.1	59.9	41.4	33.71	13.10	6.04	58.72	80.1
$BeO(c) + AlCl_3(g) = AlOCl(g) + BeCl_2(g)$	93.1	73.9	55.4	40.71	16.16	8.07	74.11	101.0
$NiO(c) + AlCl_3(g) = AlOCl(g) + NiCl_2(g)$	74.3	51.2	28.8	32.48	11.21	4.20	61.68	84.1

*The free energy for the reaction at 2400°K per mole of AlOCl(g) is 29.2 K.cals.mole^{-1}

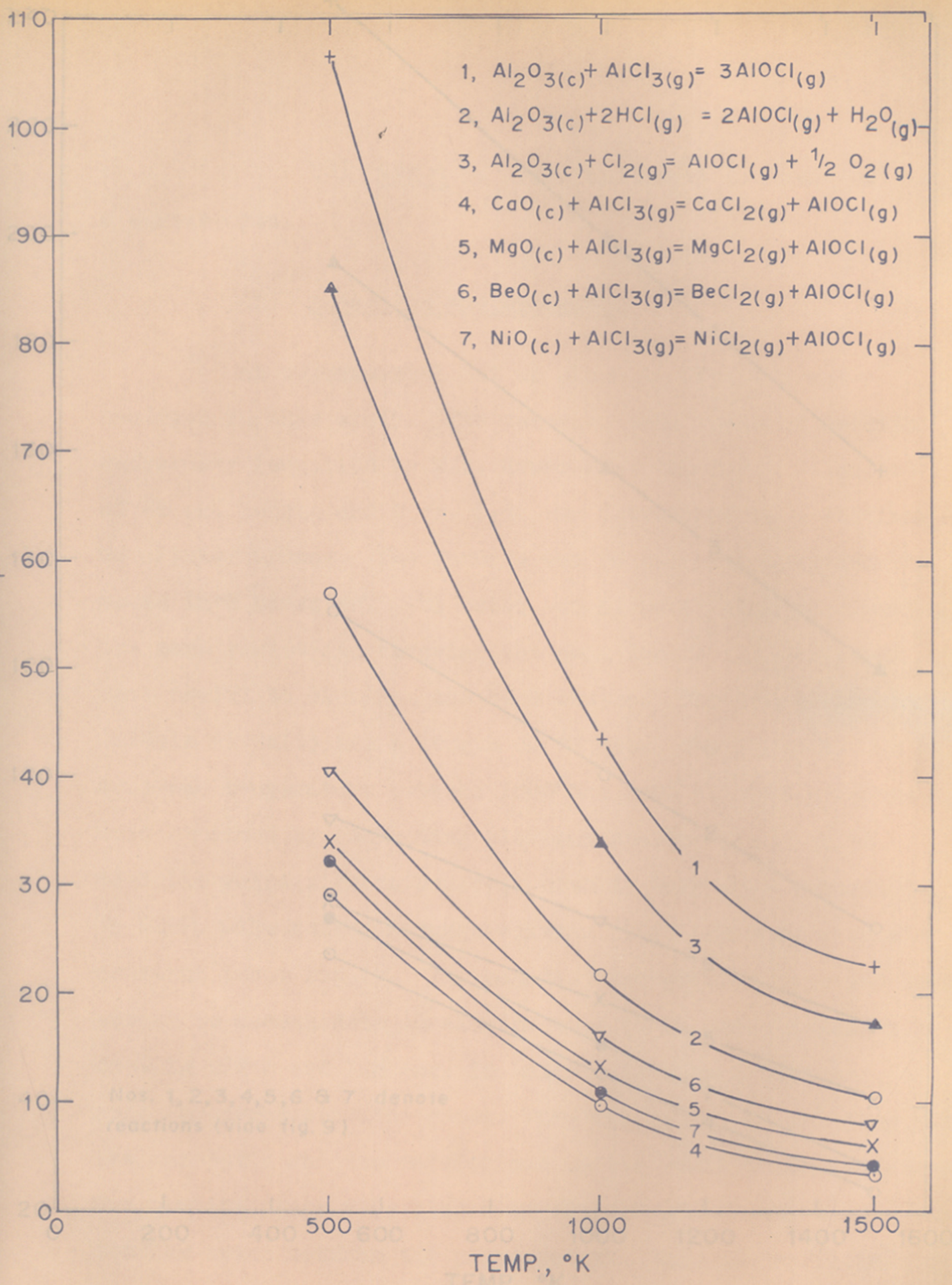

FIG. 9. PLOT OF $-\log K_P$ VS TEMPERATURE FOR VARIOUS REACTIONS.

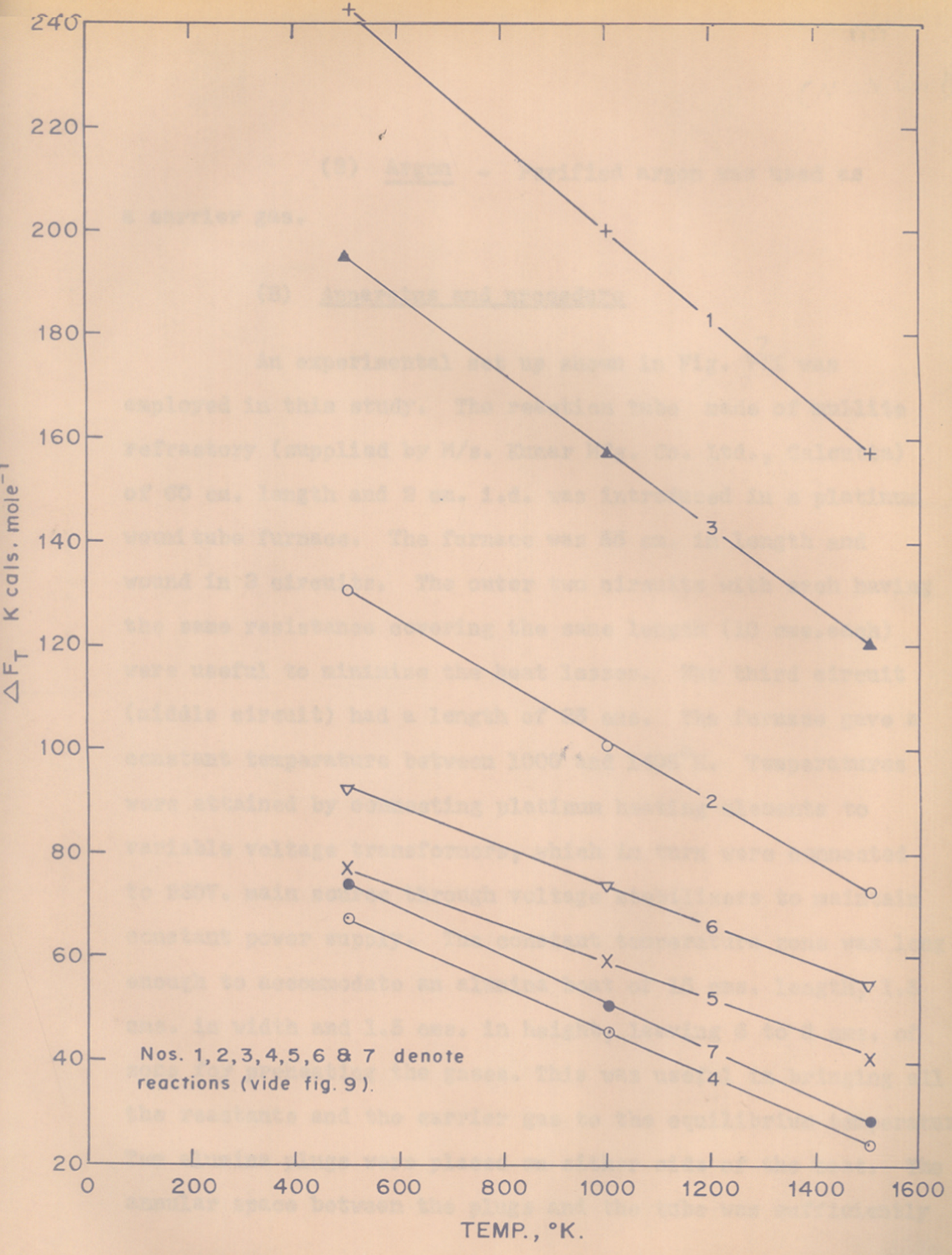

FIG. 10. CHANGE OF ΔF_T VS TEMPERATURE FOR VARIOUS REACTIONS.

(3) Argon - Purified argon was used as a carrier gas.

(B) Apparatus and procedure

An experimental set up shown in Fig. ~~VII~~ 7 was employed in this study. The reaction tube made of mullite refractory (supplied by M/s. Kumar Mfg. Co. Ltd., Calcutta) of 60 cm. length and 2 cm. i.d. was introduced in a platinum wound tube furnace. The furnace was 55 cm. in length and wound in 3 circuits. The outer two circuits with each having the same resistance covering the same length (10 cms.each) were useful to minimize the heat losses. The third circuit (middle circuit) had a length of 25 cms. The furnace gave a constant temperature between 1000 and 1498°K. Temperatures were attained by connecting platinum heating elements to variable voltage transformers, which in turn were connected to 230V. main source through voltage stabilizers to maintain constant power supply. The constant temperature zone was long enough to accommodate an alumina boat of 15 cms. length, 1.5 cms. in width and 1.5 cms. in height, leaving 6 to 8 cms. of zone for preheating the gases. This was useful in bringing all the reactants and the carrier gas to the equilibrium temperature. Two alumina plugs were placed on either side of the boat. The annular space between the plugs and the tube was sufficiently

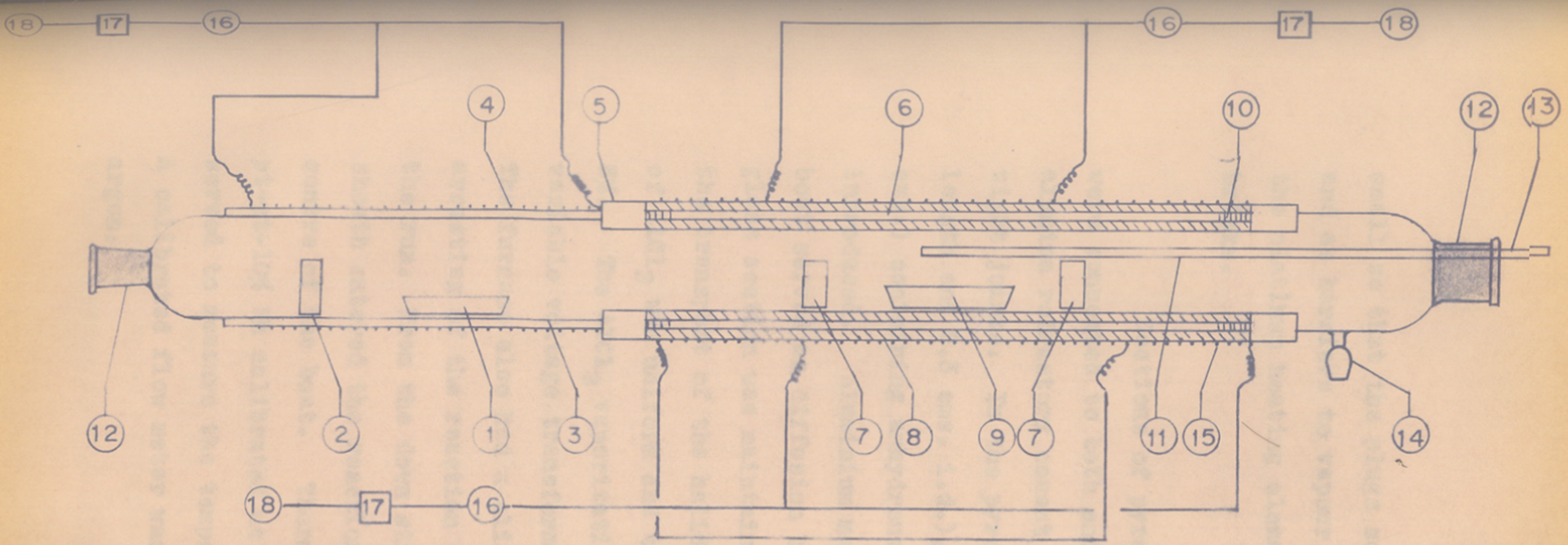

FIG. 7. A SCHEMATIC DIAGRAM OF TRANSPIRATION APPARATUS.

1	$AlCl_3$ BOAT
2	ALUMINIUM METAL SHIELDS
3	PYREX GLASS ASSEMBLY ($AlCl_3$ VAPORIZATION CELL)
4	HEATING ELEMENTS (NICHROME)
5	CEMENTED JOINTS
6	REACTION TUBE (MULLITE)
7	ALUMINA SPACERS
8	FURNACE CORE
9	SAMPLE BOAT
10	SUPPORTS FOR REACTION TUBE
11	THERMOCOUPLE PROTECTION TUBE
12	B_{29} GLASS JOINT
13	SILICA SHEATH SERVING AS COLD FINGER
14	TO COLLECTOR
15	HEATING ELEMENTS (PLATINUM)
16	VARIABLE VOLTAGE TRANSFORMER
17	CONSTANT VOLTAGE STABILIZER
18	POWER SUPPLY

small so that the plugs served both as radiation shields and as barriers to vapour diffusion. The insulation around the platinum heating elements consisted of light magnesia bricks.

Sections of pyrex glass tubing of suitable sizes were connected to both ends of the reaction tube with high alumina refractory cement (Accoset-50) to give cemented gas tight joints. In the pyrex tube at the upstream end (45 cms. length and 2.5 cms. i.d.), a glass boat (1 cm. x 1 cm. x 8 cms.) containing anhydrous aluminium trichloride was introduced. Aluminium metal baffles on either side of the boat served as diffusion barriers. The temperature of the glass section was maintained at 150 ± 1°C to facilitate the transport of the halide by argon gas. Thus the supply of $AlCl_3$ was uniform and the deviation was not more than 5%. The $AlCl_3$ vaporization furnace was connected to a variable voltage transformer through a voltage stabilizer. The furnace also had a sliding arrangement to facilitate the arresting of the reaction quickly by pushing it out after the run. From the down stream end a mullite thrmocouple sheath entered the reaction tube and was positioned over the centre of the boat. Thermocouples of chromel-alumel, and pt-pt-10% Rh calibrated at various points (m.p. of Al, Cu) served to measure the temperatures during the reaction. A calibrated flow meter was employed to measure the flow of argon.

Whenever solids condensed from the gaseous products were to be studied the mullite thermocouple sheath was replaced by silica sheath (the end of which was in the colder zone) figure VIII. The silica sheath served as an air cooled cold finger.

In these experiments the carrier gas saturated with $AlCl_3$ was allowed to react with NiO(c) under equilibrium conditions. The products in the boat after the reaction were identified by x-ray and spectrographic methods. The amount of NiO taking part in the reaction was determined by the chemical analysis of the products in the boat.

The gaseous products of the reaction carried away by the argon gas were condensed on the cold finger. After the experimental run of one hour the heating of $AlCl_3$ was stopped (arresting the flow of $AlCl_3$) and the system was cooled in the argon gas flow. The boats were passed to a chamber containing dry nitrogen and weighed. The residue in the alumina boat was powdered in a dry box and analysed for NiO and $NiAl_2O_4$.

4.3. IDENTIFICATION OF THE PRODUCTS

The residue in the boat was examined by studying the x-ray powder patterns of the solids. A sample of the residue ground to fine size was introduced in a glass capillary

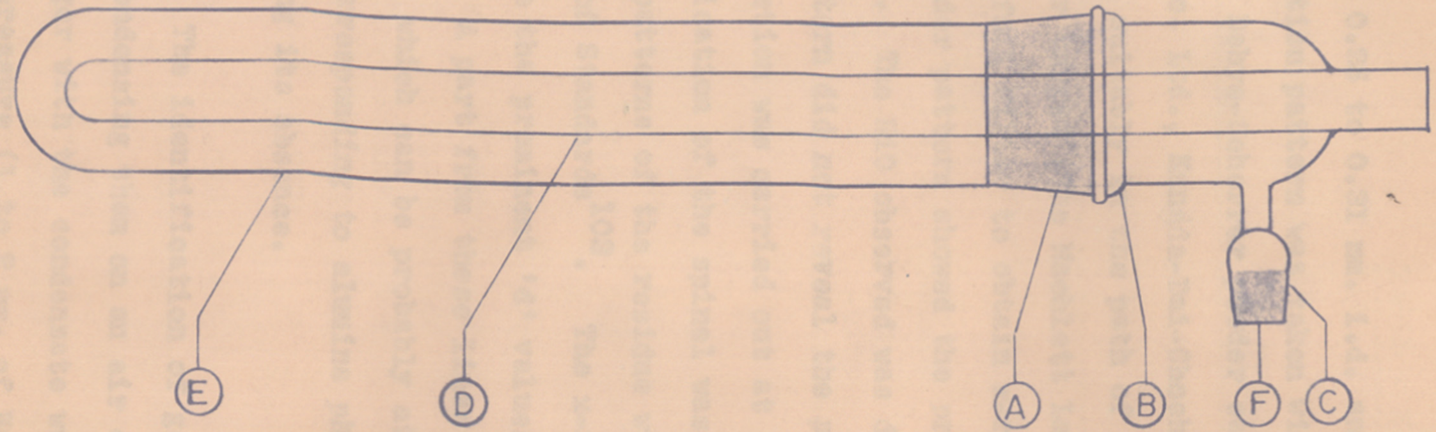

FIG. 8. COLD FINGER (AIR COOLED)

A, B — B_{29} MALE AND FEMALE JOINTS
C — B_{24} MALE GLASS JOINT
D — SILICA TUBE
E — QUARTZ TUBE
F — VACUUM CONNECTION

tube of 0.25 to 0.31 mm. i.d. and the photograph of the diffraction pattern was taken with a Debye-Scherrer camera (Regaku Debye-Scherrer powder camera, 90 mm. dia., Ragoka Denki Co. Ltd., Kanada-Dai-Chochigada-KW, Tokyo, Japan) mounted suitably in the path of the x-rays. The unit had a copper target (The Machlett Laboratories Inc., USA) with nickel foil filter to obtain x-ray beam at 50 KV and 18 mA. The powder pattern showed the presence of NiO and the spinel $NiAl_2O_4$. The NiO observed was due to the unreacted material. The pattern did not reveal the presence of Al_2O_3 even when the reaction was carried out at lower temperatures. The identification of the spinel was possible by comparing the powder patterns of the residue with that given by the National Bureau of Standards[103]. The x-ray data is given in Table X in which the prominent 'd' values for NiO and $NiAl_2O_4$ are shown. A part from these lines a few very faint lines were observed which can be probably attributed to the impurities. Lines corresponding to alumina phase were not present indicating its absence.

The identification of gaseous products was carried out by condensing them on an air cooled silica sheath. The cold finger with the condensate was heated at 800°C under ~~a~~ reduced pressure (1 to 2 mm. of Hg). During the initial

TABLE - X

PROMINENT X-RAY DIFFRACTION LINES OF THE PRODUCTS OF REACTION (75)

Time of exposure : 2 hours.
Radiation : Cu K (1.5405A).

$NiAl_2O_4$(c)				NiO(c)			
Experimental		N.B.S.Standard		Experimental		N.B.S.Standard	
d^{o}A	Intensity	d^{o}A	Intensity	d^{o}A	Intensity	d^{o}A	Intensity
4.7460	W	4.650	22	2.4249	S	2.410	91
2.8535	W	2.846	22	2.0914 2.0529	S^{++}	2.088	100
2.4161	S^{++}	2.427	100				
2.1119 2.0204	S	2.013	63	1.483	M	1.476	57
				1.2664	W	1.259	16
1.6504	VW	1.6415	7	1.2151	W	1.206	13
1.5560	M	1.5485	29	1.0491	VW	1.0441	8
1.4899	S	1.4232	60	1.4324	M	0.9582	7
1.4285	S	1.3601	< 1	0.9428	W	0.9338	21
1.2661	VW	1.2739	< 1	0.8587	VW	0.8527	15
1.2148	VW	1.2274	8			0.8040	7
1.0496	M	1.2134	< 1				
0.94018	VW	1.1613	6				
		1.0753	2				
		1.0476	11				
		1.0061	7				
		0.9291	7				
		0.8998	6				
		0.8214	15				

stages (i.e. at 150°C) all the $AlCl_3$ sublimed off and the temperature was increased to 800°C, when all the nickel chloride sublimed off leaving behind white powder on the cold finger. X-ray and chemical analysis of the powder showed it to be Al_2O_3. It is possible that Al_2O_3 was formed due to the dissociation of AlOCl according to the equation

$$3AlOCl = Al_2O_3(c) + AlCl_3(g) \qquad \ldots[74]$$

4.4. POSSIBLE EQUILIBRIUM REACTIONS

Considering nickel aluminate, nickel chloride as the products the following stoichiometric reactions can be written:

$$6NiO(c) + 4AlCl_3(g) = NiAl_2O_4(c) + 5NiCl_2(g) + 2AlOCl(g) \ldots[75]$$

$$4NiO(c) + 2AlCl_3 = NiAl_2O_4 + 3NiCl(g) + 1\tfrac{1}{2}Cl_2 \quad \ldots[76]$$

Reaction 76 can be rejected on the basis that chlorine is not observed during the course of the reaction. Consequently the reaction 75 has been given consideration. Here it may be pointed out that the reaction 75 can be said to consist of the reaction 73 and twice the reaction 71.

4.5. ANALYSIS OF THE PRODUCTS

The azure coloured product obtained in the boat together with the excess nickel oxide was finely ground. The fine powder was fused with potassium pyrosulfate in a silica crucible (ratio : $K_2S_2O_8$: substance = 20:1). After the substance was fused completely, the crucible with the contents was cooled and the solid mass was treated with 1N sulphuric acid and was made to a definite volume. About 25 ml. of the aliquot was taken and aluminium was determined gravimetrically as alumina by standard methods. The filtrate remaining after the separation of aluminium hydroxide was treated with dilute HCl and concentrated. Nickel was determined in the concentrate by the dimethyl glyoxime method. From the alumina obtained, the corresponding $NiAl_2O_4$ was calculated and the amount deducted from the total weight of the substance after the experiment. This gave the weight of unreacted NiO. NiO reacted was calculated from the initial weight of NiO and the weight of unreacted NiO. In a few experiments the substance deposited in the colder parts was collected and carefully sublimed under reduced pressure and the condensate was weighed. The quantity of nickel dichloride thus obtained was used to determine the extent of the reaction. In a few experiments alumina collected on the colder parts was also quantitatively determined.

4.6. TREATMENT OF THE DATA

The vapour pressures of $NiCl_2(g)$, $AlCl_3(g)$ and $AlOCl(g)$ were calculated from the experimentally determined weight loss of NiO, in the reaction 75. Assuming that the ideal gas law holds good in the equilibrium zone, the partial pressures of the various components were calculated as follows:

$$P_{NiCl_2} = \text{Pressure of nickel chloride generated :}$$
$$= 5/6\ X n_{NiO} \times RT_r/V_r \qquad \ldots[77]$$
$$P_{AlCl_3} = (n_{AlCl_3} - 4/6\ n\ NiO) RT_r/V_r \qquad \ldots[78]$$
$$P_{AlOCl} = 2/6\ n_{NiO} \times RT_r/V_r \qquad \ldots[79]$$

where P_{NiCl_2}, P_{AlCl_3} and P_{AlOCl} denote the partial pressures of the respective components and V_r represents the volume of the flow gas passed at the room temperature T_r and R being the gas constant. nNiO and $nAlCl_3$ denote the number of moles of the respective components.

The equilibrium constant K_p was calculated from the above equilibrium partial pressures

$$K_p = \frac{(P^2 AlOCl)(P^5 NiCl_2)}{(P^4 AlCl_3)} \qquad \ldots[80]$$

The experimental results and the calculated equilibrium constants are given in the Table XI. It may be stated that the dimer $Al_2Cl_6(g)$ is not an important species at these temperatures of study.

TABLE - XI

TRANSPIRATION DATA AND THE CALCULATED EQUILIBRIUM CONSTANTS FOR THE REACTION

$6NiO(c) + 4AlCl_3(g) = NiAl_2O_4(c) + 5NiCl_2(g) + 2AlOCl(g)$

Temp. °K	Flow rate L/hr.	$AlCl_3$ passed moles x 10^{-2}	NiO trans. moles x 10^{-2}	$NiAl_2O_4$ formed in grams	P_{NiCl_2} atmos. x 10^{-2}	P_{AlOCl} atmos. x 10^{-2}	P_{AlCl_3} atmos. x 10^{-2}	K_p	-log K_p
√(4) 1328*	3.96	1.7762	1.4930	0.4374	10.2780	4.112	6.4509	1.1194 x 10^{-3}	2.9513
(3) 1291*	3.82	3.8740	2.2710	0.6653	16.1800	6.4720	20.1770	2.8025 x 10^{-4}	3.5525
√(2) 1278	3.80	1.9140	1.3900	0.4072	7.4536	2.9814	6.3537	1.2547 x 10^{-4}	3.9014
(1) 1269	4.06	1.8168	1.4080	0.2104	7.0650	2.8260	4.2020	7.5860 x 10^{-5}	4.1200
(10) 1446	4.36	2.1360	2.7140	0.7956	12.6840	5.0736	1.8322	7.4994 x 10^{-1}	0.1250
(7) 1390	4.08	1.5952	1.8518	0.5425	9.2484	3.6994	2.1617	4.2407 x 10^{-2}	1.3725
√(8) 1397	4.42	1.8101	2.1053	0.6167	9.7056	3.8822	2.2494	5.0699 x 10^{-2}	1.2950
(5) 1357	4.10	1.8149	1.9050	0.5581	9.4677	3.7871	3.2497	9.7825 x 10^{-3}	2.0096
(6) 1376**	4.00	0.6361	0.8525	0.2498	2.1714	0.8686	0.2073	1.9734 x 10^{-2}	1.7048
(9) 1437	4.34	1.2146	1.6140	0.4728	7.5779	3.0311	0.7809	6.1741 x 10^{-1}	0.2094

* Reactions were carried out for 45 minutes.

** Reaction was carried out for 2 hours and the $AlCl_3$ furnace was kept at 146°C.

4.7. RESULTS AND DISCUSSION

The free energies are calculated by the equation

$$\Delta F^{\circ} = -RT\ln K_p \qquad \ldots[27]$$

From the plot of log K_p vs 1/T (Fig. XI) the value for the second law heat 190.05 ± 5.04 Kcals. $mole^{-1}$ is obtained. This value is at the mean temperature of $1360^{\circ}K$. As the heat content functions of $NiAl_2O_4$(c) are not available, they are assumed to be similar to those of $FeAl_2O_4(c)^{102*}$ and the heat of reaction at $298^{\circ}K$ has been obtained as follows:

$$\Delta H^{\circ}_{1360} = 190.05 \pm 5.04 \text{ Kcals. mole}^{-1}.$$

C_p values for NiO(c), $FeAl_2O_4$(c) are taken from Kelley.

C_p values for AlOCl(g), $AlCl_3$(g) are taken from $JANAF^{104}$ tables.

C_p value of $NiCl_2$(g) is taken as 14 cals.$deg.^{-1}$.$mole^{-1}$.

(The heat capacity of $NiAl_2O_4$(c) is also taken as the sum of the heat capacities of NiO(c) and Al_2O_3(c) at the required temperature. The difference in the values of ΔH°_{298} calculated by this and that calculated by assuming the C_p values of $FeAl_2O_4$(c) is only 0.3 Kcals. $mole^{-1}$).

$$\Delta C_p = -24.906 + 14.57 \times 10^{-3}\,T.$$

* Both being invert spinels and having the same structure

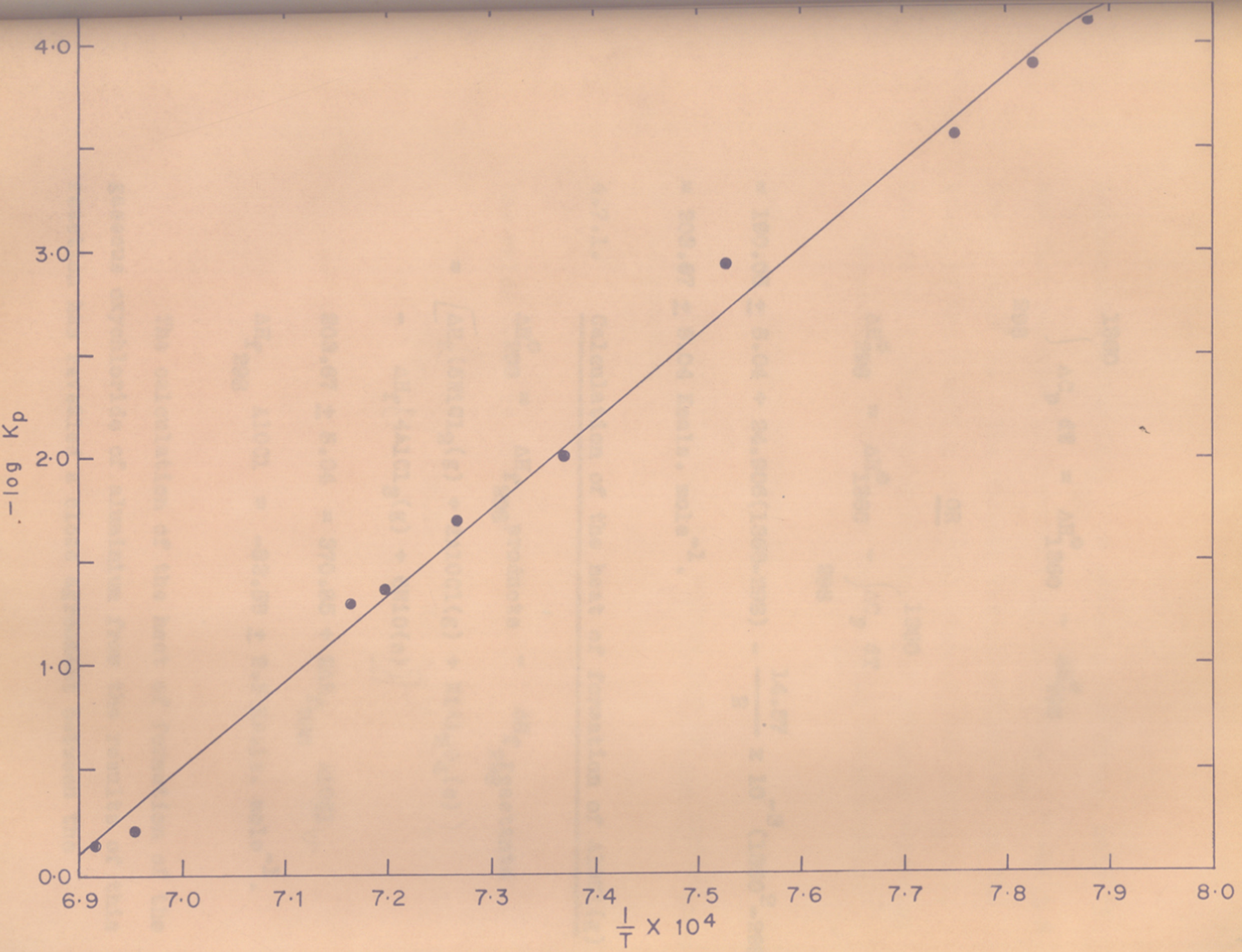

FIG. 11. PLOT OF $-\text{LOG}\ K_p$ VS $\frac{1}{T} \times 10^4$ FOR THE REACTION
$6\,NiO_{(c)} + 4\,AlCl_{3(g)} = NiAl_2O_{4(c)} + 5\,NiCl_{2(g)} + 2\,AlOCl_{(g)}$

$$\int_{298}^{1360} \Delta C_p \, dT = \Delta H^o_{1360} - \Delta H^o_{298}$$

<u>OR</u>

$$\Delta H^o_{298} = \Delta H^o_{1360} - \int_{298}^{1360} \Delta C_p \, dT$$

$$= 190.05 \pm 5.04 + 24.906(1360-298) - \frac{14.57}{2} \times 10^{-3}(1360^2-298^2)$$

$$= 203.67 \pm 5.04 \text{ Kcals. mole}^{-1}.$$

4.7.1. Calculation of the heat of formation of AlOCl(g)

$$\Delta H^o_{298} = \Delta H_{f_{298}} \text{products} - \Delta H_{f_{298}} \text{reactants}$$

$$= \Big[\Delta H_f\big(5NiCl_2(g) + 2AlOCl(g) + NiAl_2O_4(c)\big)$$

$$- \Delta H_f\big(4AlCl_3(g) + 6NiO(c)\big)\Big]$$

$$203.67 \pm 5.04 = 370.85 + 2\Delta H_{f_{298}} \text{ AlOCl}_{(g)}$$

$$\Delta H_{f_{298}} \text{ AlOCl} = -83.59 \pm 2.5 \text{ Kcals. mole}^{-1}.$$

The calculation of the heat of formation of the gaseous oxychloride of aluminium from the results of this reaction has revealed a close agreement between the experimental value ($\Delta H_{f_{298}}$ = -83.59 ± 2.5 Kcals. mole^{-1}) and that reported by Greenbaum <u>et.al</u>.[100] ($\Delta H_{f_{298}}$ = -84 ± 5 Kcals. mole^{-1}). The present transpiration work on the study of the reaction of NiO(c) with gaseous $AlCl_3$ has, therefore, brought forth the important evidence regarding the presence of AlOCl(g) at the reaction temperatures.

4.8. ENTROPY OF REACTION

By substituting the values for ΔF_{1360} and ΔH_{1360} in the equation

$$\Delta F_T = \Delta H_T - T\Delta S \qquad \ldots[58]$$

the value of ΔS is obtained

$$\Delta S_{1360} = 130.63 \pm 3.7 \text{ cals. deg.}^{-1} \text{ mole}^{-1}.$$

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TABLE - XII

Thermodynamic data for the reaction

$6NiO(c) + 4AlCl_3(g) = NiAl_2O_4(c) + 5NiCl_2(g) + 2AlOCl(g)$

Second Law Method

ΔH_r at 1360 = 190.05 ± 5.04 K.cals. $mole^{-1}$

ΔS_r at 1360 = 130.63 ± 3.7 Cals. $deg.^{-1}$ $mole^{-1}$

ΔH_r at 298 = 203.67 ± 5.04 K.cals. $mole^{-1}$

ΔH_f at 298 for AlOCl(g) = -83.59 ± 2.5 K.cals.$mole^{-1}$

CHAPTER - 5

STUDY OF THE REACTIONS OF NICKEL CHLORIDE WITH

[I] : CERIUM SULPHIDE(Ce_2S_3)
AND
[II] : MOLTEN ALUMINIUM

CHAPTER - 5

STUDY OF THE REACTIONS OF NICKEL CHLORIDE WITH
(I) CERIUM SULPHIDE (Ce_2S_3) AND
(II) MOLTEN ALUMINIUM

5.1. In the previous chapters it has been shown how the simple transpiration technique acts as a valuable aid for the studies of equilibrium reactions involving unstable gaseous molecules like NiCl and AlOCl. It is, therefore, thought worthwhile to employ the above technique in the studies of complicated reactions in which a number of gaseous products are involved. The experimental work for these reactions is described in the present chapter.

SECTION : I

STUDY OF THE REACTION OF $NiCl_2(g)$ WITH $Ce_2S_3(s)$

5.1.1. Sulphides of rare earths are highly refractory but extremely sensitive to oxygen. These sulphides when heated in air dissociate giving free sulphur and an oxysulphide. Except for a few monosulphides almost nothing is known about their thermodynamic properties at high temperatures.

Senderoff **et.al.**[105] have prepared pure 99.2% cerium chloride by chlorinating sesquisulphide of cerium at 300°C. The advantage in this method is that no oxychloride is formed. Initially a few preliminary experiments were carried out by heating equimolar mixtures of $NiCl_2$ and Ce_2S_3 in an evacuated sealed quartz tube at a temperature of 750°C. The products on analysis showed the presence of nickel metal, cerium trichloride and free sulphur. The reaction may be represented as:

$$Ce_2S_3(s) + 3NiCl_2(s) = 3Ni(s) + 2CeCl_3(l) + 1\frac{1}{2} S_2(g) \quad ..[81]$$

Experiments were carried out together with the identification and analysis of the products to study the reaction mechanism.

5.1.2. Experimental

(A) Materials

1. Nickel chloride - Pure anhydrous nickel dichloride (purification discussed earlier) was used in this study.

2. Cerium sesquisulphide - Cerium sesquisulphide was prepared by sulphiding the oxide of cerium with carbondisulphide. Pure dry nitrogen was used as a carrier gas to transport carbon disulphide vapours to the hot zone where they reacted with cerium oxide (AR quality supplied by the Atomic Energy Establishment, Trombay,Bombay) kept at

1000°C. The reaction may be represented by the following equation:

$$2CS_2(g) + 2CeO_2(c) = Ce_2S_3(c) + 2CO(g) + SO_2(g) \quad \ldots [82]$$

The sulphidation reaction was carried out for 2 hours to get complete conversion of the oxide into sulphide. Details of this method are given by Ya Markouski <u>et.al.</u>[106]. The product obtained by this method contained some adsorbed free sulphur. In order to remove the free sulphur the sesquisulphide was heated at 700°C in an atmosphere of argon for about an hour. The argon gas was previously purified to remove the traces of oxygen by the method given by Atchayya <u>et.al.</u>[107]. The sesquisulphide was analysed for cerium (as ceria by the gravimetric method) and sulphur (by fusion with Na_2O_2 in nickel crucible converting it to sulphate). The analysis gave 74.3% cerium and 25.88% of sulphur (required for Ce_2S_3; Ce = 74.45%, S = 25.55%).

(3) Argon - Argon was used as a carrier gas and its purification has been described in Chapter 3.

(B) Apparatus and Procedure

The experimental set up and the procedure were similar to that described in Chapter 3. The alumina boat containing Ce_2S_3 was heated to the required temperature in the zone K_2 in an argon atmosphere. When the temperature in the two zones got stabilized, nickel chloride was introduced in the zone K_1 and the experiment was started taking the usual precautions to avoid contamination of the carrier gas with air. The experiment was carried out for a definite period of time and the heating of $NiCl_2$ was stopped thereby arresting the reaction. The system was cooled in an argon atmosphere and the boats containing the sesquisulphide and the nickel halide were pushed to a chamber containing dry nitrogen gas and were weighed.

5.2.3. IDENTIFICATION OF THE PRODUCTS

The residue in the boat was heated with concentrated nitric acid. The sulphide reacted with the acid with the evolution of hydrogen sulphide. The solution was filtered and the filtrate on analysis showed the presence of nickel and cerium. The residue left on the paper was dried and ignited. Sulphur dioxide vapours were observed while heating, whereas no residue was left in the crucible. Hence the solid that produced sulphur dioxide must be the free sulphur.

The identification of the gaseous products was made by condensing the outcoming gases on an air cooled silica sheath (cold finger). Free sulphur was found on the colder parts of the reaction tube. Nickel metal globules were observed on the radiation shields.

5.1.4. ANALYSIS OF THE PRODUCTS

The residue in the boat was weighed and heated with 0.2NHNO_3. The sulphur from the unreacted Ce_2S_3 escaped as hydrogen sulphide. The solution was filtered. The analysis of the residue and the filtrate was carried out as given below:

Residue - The residue was washed with water and treated with 6N HNO_3 and the solution was warmed till complete dissolution occurred. Nickel in the solution was estimated by dimethyl glyoxime.

Filtrate - The filtrate containing the cerium chloride was made up to a known volume. An aliquot was taken and chloride was determined by Volhard's method. To another portion of the aliquot excess ammonium chloride and ammonium hydroxide were added and the solution warmed. The precipitated cerium hydroxide was filtered, dried, ignited and weighed as ceria. The filtrate after separating cerium hydroxide, was treated with dilute hydrochloric acid. This solution was treated with dimethyl glyoxime followed by ammonia. In some experiments very small amount of nickel was detected. This was determined and added to the nickel value obtained from the analysis of the first residue.

5.1.5. TREATMENT OF THE DATA - RESULTS AND DISCUSSION

From the amount of chloride, cerium trichloride formed was calculated. Nickel dimethyl glyoxime complex gave the amount of nickel obtained in the experiment. These two when subtracted from the final weight of the residue left in the boat after the experiment gave the amount of unreacted cerium sesquisulphide. The experimental data and the analytically determined quantities of cerium chloride, nickel metal and the reacted cerium sulphide are tabulated in Table XIII. From the tabulated data it can be seen that the cerium chloride obtained was almost equivalent to the cerium sulphide reacted (1 mole of $Ce_2S_3 \equiv 2$ moles of $CeCl_3$). The amount of nickel metal deposited was about 3 to 4 times that of the sulphide consumed. From the above experimentally determined quantities the following stoichiometric reaction may be considered:

$$Ce_2S_3(s) + 3NiCl_2(g) \; = \; 2CeCl_3(l) + 3Ni(c) + 1\tfrac{1}{2}\,S_2(g) \quad \ldots[83]$$

However, a few side reactions are also possible at these temperatures and in view of the experimental evidence they are discussed below:

(1) Deposits of nickel metal have been observed on the radiation shields as well as on the cold finger. This may

TABLE - XIII

EXPERIMENTAL RESULTS OF THE REACTION OF $Ce_2S_3(s)$ WITH $NiCl_2(g)$

Temp. °K	Flow rate Liter/hr.	$NiCl_2$ passed moles x 10^2	Ce_2S_3 reacted moles x 10^3	$CeCl_3$ obtained moles x 10^3	Ni deposited in gm.
1394	4.42	0.4266	1.0630	2.1145	0.1903
1291	4.76	0.6522	1.5450	3.0908	0.2644
1324	5.44	2.1700	2.1130	4.2172	0.40735
1420	4.32	3.2150	3.7610	6.895	0.80825
1326	4.16	1.1500	3.1510	6.2950	0.6460
1227	4.60	3.2730	2.880	5.7606	0.60085

be due to the disproportionation of gaseous nickel monochloride formed according to the equation:

$$Ni(c) + NiCl_2(g) = 2NiCl(g) \qquad ...[\ 1\ ]$$

(2) About 2% loss in the quantity of cerium can be attributed to the vaporization of cerium chloride ($CeCl_3$) at the reaction temperatures[108]

$$CeCl_3(l) \longrightarrow CeCl_3(g) \qquad ...[84]$$

(3) The solubility of metals in molten halides also produce halides of lower valent states[109]. The temperatures at which the present reaction has been studied are quite high and hence the reaction between nickel metal and molten cerium chloride ($CeCl_3$) can be considered as follows:

$$Ni(c) + CeCl_3(l) = NiCl(g) + CeCl_2 \qquad ...[85]$$

The gaseous monovalent nickel chloride (NiCl) is quite well known but the thermodynamic stability of the lower valent chloride of cerium ($CeCl_2$) has not been known.

SECTION : II

REACTION OF NICKEL CHLORIDE WITH MOLTEN ALUMINIUM

5.2. INTRODUCTION

The reducing action of aluminium metal is known since a long time. The well known Thermite or Goldschmidt process for preparing metals and alloys is the exothermic reaction caused by the reduction of an oxide by aluminium metal according to the equation:

$$3MeO(c) + 2Al(1) = 3Me(1) + Al_2O_3(c) \quad ...[86]$$

Reactions of aluminium metal with chlorine and gaseous aluminium chloride are well known. The reduction of the oxides of calcium, barium and strontium with molten aluminium is described by Zhukovatskii[110] giving the thermodynamics of the reduction processes. Review on aluminium as a reducing agent in metallurgy is available in the literature. The stepwise reduction of titanium tetrachloride to titanium metal is described by Balduin[111] in his studies on the reduction of metal halides with molten aluminium:

$$TiCl_4(g) + Al(l) = AlCl_3(g) + 3TiCl_3(g) \quad ...[87a]$$

$$TiCl_3(g) + Al(l) = AlCl_3(g) + 3TiCl_2(g) \quad ...[87b]$$

$$TiCl_2(g) + 2Al(l) = 2AlCl_3(g) + 3Ti(s) \quad ...[87c]$$

The formation of $AlCl_3(g)$ and titanium metal is having negative free energy thereby indicating the ease of the reaction but as the temperature increases the formation of $TiCl_3(g)$ is more favoured as indicated by the free energy changes. The solubilities of salts in molten metals are given by Yosim and Luchsinger[109]. When a metal is allowed to react with its halide, a gaseous subhalide is formed (via. $Al + AlCl_3 = 3AlCl$; $Mn + MnCl_2 = 2MnCl$; $Ni + NiCl_2 = 2NiCl$). The aim of the present work is to study the reaction of gaseous nickel chloride with molten aluminium metal at high temperatures.

Balduin[111] in his studies on the reduction of metal chlorides to metals with aluminium has calculated the free energies per atom of chlorine for the reactions 88 and 89:

$$NiCl_2(g) + 2Al(l) = 2AlCl(g) + Ni(c) \quad ...[88]$$

$$3NiCl_2(g) + 2Al(l) = 2AlCl_3(g) + 3Ni(c) \quad ...[89]$$

A few other reactions (reactions 90, 91 and 92) are possible in this system. Their feasibilities and thermodynamic properties are discussed in the present work:

$$NiCl_2(g) + Al(l) = AlCl_2(g) + Ni(c) \qquad ...[90]$$

$$NiCl_2(g) + Al(l) = AlCl(g) = NiCl(g) \qquad ...[91]$$

$$2NiCl_2(g) + 2Al(l) = 2AlCl(g) + Ni(c) + 1/2\ Cl_2 + NiCl(g) \qquad ...[92]$$

The free energies represented in the Table XIII suggest that the reactions 88 and 89 are equally feasible as these values (i.e. free energy values) per gram atom of chlorine of the reducedchloride are almost the same. Chai <u>et.al.</u>[112] have carried out the reaction of Al with $AlCl_3(g)$ at 800-1000°K and calculated the thermodynamic quantities for the reaction 93 and 94:

$$2AlCl_3(g) + Al(l) = 3AlCl_2(g) \qquad ...[93]$$

$$2AlCl_2(g) = Al_2Cl_4(g) \qquad ...[94]$$

However, at temperatures above 1000°K, $AlCl_2(g)$ is not a major species. The values calculated by Irman[113] show that $AlCl_2(g)$ is relatively less stable as compared to $AlCl(g)$ at high temperatures. Hence, in this study the reaction 90 is rejected.

TABLE - XIV

SEVERAL POSSIBLE REACTIONS OF MOLTEN ALUMINIUM WITH $NiCl_2(g)$

Reaction	$\Delta H_{r_{298}}$ in Kcals.mole	$-(\Delta F_T)$ Free energies per gm. atmos. of chloride reduced in Kcals.					
		1000°K	1100°K	1200°K	1300°K	1400°K	1500°K
$2Al(l) + 3NiCl_2(g) = 2AlCl_3(g) + 3Ni(c)$	-243.2	29.40	28.29	27.21	26.11	24.98	23.81
$2Al(l) + NiCl_2(g) = 2AlCl(g) + Ni(c)$	- 13.5	18.06	19.09	20.09	21.06	21.93	22.78
$Al(l) + NiCl_2(g) = AlCl_2(g) + Ni(c)$	- 54.7	23.83	23.48	23.10	22.70	22.25	21.77
$Al(l) + NiCl_2(g) = AlCl(g) + NiCl(g)$	+ 38.7	-	-	-	-	-	-
$2Al(l) + 2NiCl_2(g) = 2AlCl(g) + NiCl(g) + Ni(c) + \frac{1}{2}Cl_2(g)$	+ 38.8	-	-	-	-	-	-

5.2.1. Experimental

(A) Materials

1. Nickel dichloride - Pure anhydrous nickel dichloride (method and purification described in Chapter 3, Section I - Sublimation of $NiCl_2$) was used in these studies.

2. Aluminium metal - Aluminium wire having a purity of 99.98% (BDH AR grade) was melted in argon atmosphere to expel the dissolved gases and the resulting ingot was cut into chips of suitable sizes. These chips were degreased and used in the study. The spectrographic analysis showed that the metal contains trace impurities (200 ppm. of Fe, Cu and Si).

3. Argon - Purified argon was used as a carrier gas. The details of purification are discussed earlier.

(B) Apparatus and Procedure

The experimental set up was similar to that described in the previous section. The refractory boat containing aluminium metal was positioned in zone K_2(Fig.IX Chapter III) and heated in the reaction temperature in a slow current of argon gas. When the temperature in the system reached the desired value and got stabilized the boat containing $NiCl_2$ was introduced in zone K_1. Usual precautions were taken to avoid contamination of the carrier gas with air while introducing and removing the boat from the system. The rate of argon was brought to the desired value (equilibrium flow rate) and the experiment was started. After running the experiment for a definite period of time the heating of $NiCl_2$ was stopped and the system was allowed to cool in argon atmosphere.

5.2.2. ATTACK OF AlCl(g) ON THE CONTAINER MATERIAL AND ON THE BOAT

In a few preliminary experiments it was observed that the refractory boat (weight about 10 gm.) increased in weight at the end of an experimental run of 2 hours. After each succeeding run the increase in weight progressively reduced. The boat showed almost negligible increase in weight after a total period of 18 to 20 hours. Blank experiments were carried out with $NiCl_2$ without Al and vice versa. These runs showed no appreciable increase in weight of the boat. In addition to the attack on the boat, the inner surface of the reaction tube got covered with a thin layer of black refractory material. To ensure complete passivation of the inner surface of the tube and the boat, a series of experiments were carried out by placing a number of boats containing the metal throughout the length of the tube. Consistent results were obtained only after the two surfaces were passivated satisfactorily.

A small amount of black shining product as a result of this attack was collected. The material showed no loss in weight even after heating for several hours at 1600°K. Spectrographic analysis showed the presence of silicon, iron, aluminium and nickel. As a result of this corrosive attack, the breakage of boats and tube was heavy. Only after the boat was passivated completely, the reaction was carried out.

To establish the reaction scheme the experiments were carried out at different temperatures.

5.2.3. IDENTIFICATION OF THE PRODUCTS

The residue left in the boat after the experiment revealed the presence of nickel and aluminium metals on analysis. The gaseous products formed in the reaction were carried off by argon gas and were collected in a cold trap. The substance collected in the receiver was found to be $AlCl_3$. On the colder parts of the reaction tube, aluminium metal globules were found. These may be due to the disproportionation of AlCl(g) to Al and $AlCl_3$:

$$3AlCl(g) = 2Al(l) + AlCl_3(g)$$

In a few experiments the thermocouple sheath was replaced by a silica cold finger (kept at 500 to 600°C). After the experiment the cold finger together with the condensed products when subjected to vacuum treatment (2 to 5 mm. of Hg), the chlorides of nickel and aluminium sublimed off leaving aluminium and nickel metal globules. Formation of nickel and aluminium may be due to the disproportionation of NiCl and AlCl respectively.

A careful examination of the outcoming gases revealed chlorine as it gave a positive test with a starch iodide paper. Taking into account the products formed viz. nickel as a solid and the rest NiCl, AlCl and Cl_2 as gases, the reactions 89 and 91 can be discarded. Therefore the reactions 88 and 92 are considered.

5.2.6. ANALYSIS OF THE PRODUCTS

The residue in the boat was treated with $6N HNO_3$ and warmed. When both the metals got dissolved, the solution was made up to a known volume. An aliquot of this was treated with excess NH_4Cl and NH_4OH to precipitate aluminium as hydroxide. After filtering, the precipitate was dried, ignited and weighed as Al_2O_3. Nickel in the filtrate was estimated by dimethyl glyoxime. From the amount of aluminium left in the boat, the amount of the metal reacted was calculated.

5.2.5. TREATMENT OF THE DATA

Experiments were carried out within the temperature range 1290-1418°K.

The results are tabulated in Table XV. From this data, it can be seen that the amount of nickel metal deposited is about half that of the aluminium metal reacted. This suggests two feasible reactions 88 and 92.

In addition to AlCl(g) nickel metal (deposited on the radiation shield), $AlCl_3$(g) and chlorine are also observed in the products. The presence of these several products can be explained on the basis of the side reactions as follows:

(1) The amount of aluminium metal deposited on the cold finger suggests that AlCl(g) is the major gaseous product. Aluminium trichloride collected in the receiver may be due to the disproportionation of the AlCl molecule as described earlier.

TABLE - XV

EXPERIMENTAL RESULTS OF THE REACTION OF MOLTEN ALUMINIUM WITH $NiCl_2$

Temp. °K	Flow rate Liters/hr.	$NiCl_2$ passed moles $\times 10^2$	Al reacted moles $\times 10^2$	Ni deposited in grams
1418	5.86	0.9913	0.9003	0.2562
1290	4.24	1.9810	0.8258	0.2466
1362	5.22	0.6583	0.5561	0.1722
1360	4.78	0.8803	0.6367	0.1968
1304	5.10	1.8984	0.9432	0.2976
1390	4.48	1.4354	1.1993	0.3136
1352	4.82	0.9430	0.7221	0.2152
1360	5.00	0.5527	0.1204	0.0358
1401	4.74	0.4569	0.1276	0.0352

2. The presence of nickel metal on the radiation shield indicates that NiCl(g) is also formed in the reaction giving nickel metal due to its disproportionation.

3. The chlorine produced in the reaction (equation No. 92) can react again with aluminium metal forming the aluminium halide.

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SUMMARY

SUMMARY

The high temperature chemical reactions involving Ni-$NiCl_2$, NiO-$AlCl_3$ equilibria, as well as the reactions $NiCl_2$ - Ce_2S_3, $NiCl_2$ - Al have been carried out employing the transpiration technique.

(1) Sublimation of $NiCl_2$

The sublimation pressures of nickel dichloride were determined over the temperature range 1030 and 1116°K. The experimental data gave a value of 59.33 ± 2.2 Kcals. mole^{-1}, for the heat of sublimation by the second law method. From the available thermal functions and the data obtained experimentally, the third law heat was found to be 58.52 ± 0.45 Kcals. mole^{-1}.

(2) Equilibrium reaction $Ni(c) + NiCl_2(g) = 2NiCl(g)$

Equilibrium constants were determined between the temperatures 1243 and 1398°K for the reaction. Assuming the C_p values of CuCl(g) for NiCl(g), the second law heat of reaction was calculated at 298°K from the value obtained at the mean temperature of 1320°K ($\Delta H_{r_{1320}}$ = 87.27 ± 3.1 Kcals. mole^{-1}, $\Delta H_{r_{298}}$ = 91.04 ± 3.1 Kcals. mole^{-1}). Due to the

non-availability of thermal data for NiCl(g) at different temperatures the third law heat could not be calculated. The derived heat of formation for NiCl(g) at 298°K is 38.68 ± 1.5 Kcals. mole^{-1} and is in good agreement with that reported in the literature. The entropy at 1320°K for the reaction has been calculated and it has the value 49.85 ± 7.5 cals. deg.$^{-1}$ mole^{-1}. The entropy of NiCl(g) calculated from this at 1320°K is 81.70 ± 3.7 cals. deg.$^{-1}$ mole^{-1}. There is a little difference between this value and the value calculated (77.2 cals. deg.$^{-1}$ mole^{-1}) by assuming NiCl(g) as per Brewer's Model.

(3) Reaction of $AlCl_3$(g) with NiO(c)

The reaction was carried out between the temperature range 1269° and 1446°K. The heat of reaction ($\Delta H_{r_{1360}}$ = 190.05 ± 5.04 Kcal./mole.) was obtained at the mean temperature of 1360°K. As the heat content and entropy differences at various temperatures for $NiAl_2O_4$(c) were not available, the calculations were restricted to second law only. The heat of reaction at 298°K ($\Delta H_{r_{298}}$ = 203.67 ± 5.04 K.cals. mole^{-1}) was calculated from that 1360°K by assuming the heat capacity of $NiAl_2O_4$(c) to be the sum of the heat capacities of NiO(c) and Al_2O_3(c) at the required temperatures. The heat of formation of AlOCl(g) at 298°K ($\Delta H_{f_{298}} = -83.59 \pm 2.5$ Kcals. mole^{-1}) was calculated from the heat of reaction. This value compares well with that reported in the literature ($\Delta H_{f_{298}} = -82 \pm 5$ Kcals. mole^{-1}).

(4) Reaction of Ce_2S_3 with $NiCl_2$

The reaction was carried out between the temperatures 1227 and 1394°K. From the analysis of the products and the weight loss data the reaction stoichiometry is given as:

$$Ce_2S_3(s) + NiCl_2(g) = 2CeCl_3(l) + 3Ni(c) + 1\tfrac{1}{2}S_2(g)$$

Even after considering the side reaction of nickel with nickel chloride and the vaporization of $CeCl_3$ at these temperatures, it was difficult to draw satisfactory conclusion from the experimental results. This may be due to the inherent complicated nature of the system and due to the reaction of nickel metal with molten cerium chloride. Hence, the results have been employed in the study of the reaction stoichiometry.

(5) Reaction of $NiCl_2$ with molten aluminium

The reaction was studied between the temperatures 1227° and 1418°K. The experimental results suggest that the predominant reaction is

$$NiCl_2(g) + 2Al(l) = 2AlCl(g) + Ni(c).$$

The formation of $AlCl_3(g)$ and $NiCl(g)$ was explained on the basis of the side reactions. Due to the highly corrosive nature of gaseous AlCl molecule and the various side reactions, the system gets complicated. In view of this the results have been utilised to understand the nature of the reaction.

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REFERENCES

REFERENCES

1. L. Brewer and A. W. Searcy, Ann. Rev. Phys. Chem., 7, 259 (1956).

2. A. V. Grosse, Science, 140, 781 (1963).

3. H. Schäfer, "Chemische Transport Reaktionen", Verlag Chemie, GmbH. Weinheim Bergstrasse, Germany, 1962. English translation by Hans Frankfart, Academic Press, New York and London, 1964.

4. P. Gross, "The proceedings on the symposium on the refining of non-ferrous metals" published by the Institute of Mining and Metallurgy, 1960.

5. G. Grube, A. Schneider, U. Esch and M. Flad, Z.anorg.chem., 260, 120 (1949).

6. P. Gross, D. L. Levi and E. W. Dewing, British Patent 719058 (1954).

7. M. Je.Posin, A. M.Ginstting and W. W. Petschkowski, Chem. Zentr., 1820, 2669 (1965).

8. S. Tamaru and N. Ando, Z.anorg.u.allgem.chem., 195, 305 (1931).

9. S. Tamaru and H. Sakurai, Z.anorg.u.allgem.chem., 206, 49 (1932).

10. H. Spandau and E. J. Kohlmeyer, Z.anorg.chem., 254, 65 (1947).

11. C. C. Heim, Method of producing aluminium carbide, U. S. Patent No: 2,640,760 (1953).

12. K. Kauffe and K. Pschera, Z.anorg.Chem., 262, 147 (1950).

13. G. Henrich, Z.Elektrochem., 58, 183 (1954).

14. D. Bhogeswara Rao and V. V. Dadape, J. Phys. Chem., 71, 537 (1967).

15. M. V.Stackelberg, E. Schnorrenberg, R. Paulus and K. F. Spiess, Zeit. Physik. Chem., Al 75,127 (1935).

16. A. J. Ellis and W. S. Fyfe, Pure and Applied Chemistry, Australia, 7, 261 (1957).

17. G. J. Wasserburg, J. Geol., 66, 559 (1958).

18. L. I. Grossweiner and R.S. Seifert, J.Am.Chem.Soc., 74, 2701 (1952).

19. O. Glemser, G. H. Volz and B. Meyer, Z.anorg.u.allgem. chem., 292, 311 (1957).

20. J. L. Margrave, J. Phys. Chem., 60, 715 (1956).

21. C. L. LUKE, S. S. Flaschen, Anal.Chem., 30, 1406(1958).

22. F. Ullmann, "Encyclopedia der technischen chemie" 3rd edn., vol.12, p.700 (1960), Urban and Schwarzenberg Mïlnchen (1960).

23. A. E. Van Arkel, Metal Wirtschaft, 13, 405 (1934).

24. B. Lustman and F. Kerze, "The metallurgy of zirconium," McGraw Hill, New York, 1955.

25. H. Schäfer and H. J. Heitland, Z.anorg.u.allgem.chem., 304, 249 (1960).

26. G. W. Hooper and C. B. Alcock, Proc. Roy. Soc., A254,551, (1960).

27. F. W. Loomis and F. F. Watson, Phys. Rev., 48, 280 (1935).

28. W. E. Bell, M. Tagami and U. Merten, J. Phys. Chem., 65, 510 (1961).

29. W. E. Bell, M. C. Carrison and U. Merten, J. Phys. Chem., 65, 517 (1961).

30. W. E. Bell, M. Tagami and U. Merten, J. Phys. Chem., 66, 490 (1962).

31. P. W. Gilles, Ann. Rev. Phy. Chem., 12, 365 (1961).

32. L. Brewer, Experientia Suppl., 7 227 (1957).

33. A. W. Searcy in "Proceedings of the International Conference on High Temperature Technology, A silomar, California, October, 1959", McGraw Hill Book Co., New York.

34. A. W. Searcy, Survey of Progress in Chemistry, Vol.I, 1963, Chapter 2, Academic Press, New York and London.

35. J. L. Margrave "Physicochemical measurements at high temperatures" edited by J.O.M'Bockris, J. L. White and J.D. Meckenzie, Butterworth Scientific Publications Ltd., London, 1959, Chapter 10.

36. The Characterization of High Temperature Vapours - edited by J. L. Margrave. 1967

37. K. Motzfeld, J. Phys. Chem., 59, 139 (1955).

38. R. D. Freeman and A. W. Searcy, J. Chem. Phys., 22, 762 (1954).

39. K. D. Carlson - The Molecular and Viscous Effusion of Saturated Vapour - Ph.D. Thesis, Univ. Kans., Lawrence, Kansas, 1960, U.S. Atomic Energy Comm. A.N.L., 6156(1960).

40. A. W. Searcy and R. D. Freeman, J. Chem. Phys., 23, 88 (1955).

41. A. W. Searcy and R. D. Freeman, J. Am. Chem. Soc., 76, 5229 (1954).

42. W. C. Demarcus "The Problem of Knudsen Flow" Oak Ridge Gaseous Diffusion Plant - Technical Report - K-1302, Part I, II, III, 19567/57.

43. C. I. Whitman, J. Chem. Phys., 20, 161 (1952).

44. C. I. Whitman, J. Chem. Phys., 21, 1407 (1952).

45. E. W. Balson, J. Phys. Chem., 65, 1151 (1961).

46. M. Farber, J. Chem. Phys., 36, 1101 (1962).

47. A. G. Gaydon, Dissociation Energy and Spectra of Diatomic Molecules - Chapmann and Hall Ltd., London, 1953.

48. G. Herzberg, Molecular Spectra and Molecular Structure - 1 Spectra of diatomic molecules, D. Van Nostrand Co. Inc., 1951.

49. S. P. Reddy and P. T. Rao, Proc. Phys. Soc.(London), 75, 275 (1960).

50. M. G. Inghram and J. Drowart in Proc. Intern. Symposium High Temp. Technol. Standford Research Institute, Menlopark, Calif. 29, McGraw Hill Book Co. Inc., New York, N. Y. 1960.

51. G. W. Thomson - Determination of Vapour Pressure Technic of Organic Chemistry, Vol.I, Arnold Weissberger (edited: Physical methods of organic chemistry - Part I, 3rd Edn., Interscience, New York (1959), pp.401-522.

52. H. V. Regnault, Ann. Chim., 15, 129 (1845).

53. O. Kubaschewski and E. L. Evans, Metallurgical Thermochemistry, 3rd Edn., Pergamon Press, Oxford, London, Edinburgh, New York, Paris, Frankfurt (1965).

54. F. D. Richardson and C. B. Alcock - "Chemical Equilibria" Physico Chemical Measurements at High Temperature - J. O. M'Bockris (editor), Academic Press, New York(1959), pp. 135-170.

55. L. Brewer, Atomic Energy Commission Report, U.C.R.L., 762 (1950).

56. T. V. Lepore and J. R. Van Wazer - A Discussion of the Transpiration method for determining vapour pressures - M.D.D.C., 1188, U.S. Atomic Energy Commission.

57. U. Merten, J. Phys. Chem., 63, 443 (1959).

58. R. J. Ackerman, R. J. Thorn, C. Alexander and Tetenbaum, J. Phys. Chem., 64, 350 (1960).

59. H. Schäfer, H. Jacob and K. Etzel, Z.anorg.u.allgem. chem., 286, 42 (1956).

60. H. Schafer and B. Morcher, Z.anorg.u.allgem. chem., 290, 279 (1957).

61. C. P. Kempter and C. A. Tostada, Z.anorg.u.allgem.chem., 290, 238 (1957).

62. D. Bhogeswara Rao and V. V. Dadape, J. Phy. Chem., <u>70</u>, 1349 (1966).

63. K. K. Kelley, U. S. Bureau of Mines Bulletin 383(1935), reprinted in U. S. Bureau of Mines Bulletin 601, U.S. Govt. Printing Office, Washington D.C., 1962.

64. G. N. Lewis and R. Randall "Thermodynamics" revised by K. S. Pitzer and L. Brewer, McGraw Hill Book Co. Inc., New York, N. Y. 1961, p.175.

65. J. L. Margrave, J. Chem. Education, <u>32</u>, 520 (1955).

66. W. F. Giauque, J. Am. Chem. Soc., <u>52</u>, 4808 (1930).

67. M. F. Lee, J. Phy. Chem., <u>62</u>, 877 (1958).

68. D. Cubicciotti and W. Johnson, Chemical Eng. News, 36, No. 12 34 (1958).

69. J. D. Mckinley, J. Chem. Phys., <u>40</u>, 120 (1964).

70. P. Mesnage, Cr. hebd. seances. Acd. Sci., 200,2072(1935).
Ibid 201, 389(1935).
Ibid 204, 761(1937).
Ibid 204,1929(1937).

71. K. R. More, Phys. Rev., <u>54</u>, 122 (1938).

72. W. Müller, Helv. Phy. Acta., <u>16</u>, 1 (1943).

73. V.G. Krishnamurty, Ind. J. Phys., Proc. In. Assoc. Calt. Sci., <u>26</u>, 207, 429 (1952).

74. S. V. K. Rao, S. P. Reddy and P. T. Rao, Z.Physik, <u>166</u>, 261 (1962).

75. H. Schäfer and K. Etzel, Z.anorg.allg.chem., <u>300</u>, 137 (1959).

76. F. D. Rossini, D. D.Wagman and Selected Values of Chemical and Thermodynamic Properties - N.B.S. Circular No: 500, Washington DC,1952.

77. Th. L. Allen, J. Chem. Phy., <u>26</u>, 1644 (1957).

78. H. Schäfer and G. Breil, Z.anorg.Allg.Chem., <u>283</u>, 304 (1956).

79. M. Barber, J. W. Linneti and N. A. Taylor, J. Chem. Soc., 3323 (1961).

80. E. M. Bulewicz and T. M. Sugden, Trans. Far. Soc., 57, 921 (1961).

81. J. R. McCreary and R. J. Thorn, J. Chem. Phy., 48, 3290 (1968).

82. C. G. Maier, Department of the Interior, Bureau of Mines, Technical Paper 360.

83. H. Schäfer, L. Bayer, G. Breil, K. Etzel and K. Krehl, Z.anorg. allgem. chem., 278, 300 (1955).

84. H. Schafer and G. Breil, Z.anorg.allgem. chem., 283, 304 (1956).

85. O. Kubaschewski and F. E. Wittig, Z.Electrochem., 47, 433 (1941).

86. O. Kubaschewski, Z. Metalik, 41, 208 (1950).

87. R. Schoonmaker, J. Chem. Phys., 31, 1586

88. W. S. Calabaugh, J. W. Donova and R. Gilchrist, J. Rss. Natl. Bas. Sand., 52, 73 (1954).

89. A. I. Vogel - Quantitative Inorganic Analysis.

90. Wm. F. Roeser and H. T. Wensel, National Bureau of Standards, Washington DC "Methods of testing thermocouples and thermocouple materials" in temperature, its measurement and control in science and industry". Prepared under the auspecies of the American Institute of Physics with the cooperation of N.B.S., National Res. Council - Reinhold Publishing Corpn., 330 West Forty Second Street, New York, USA, p.285(1941) - reprinted in 1958.

For various scales see also : D.R.Levejoy, Temperature scales above 1000°C, printed in symposium "Chemical and Thermodynamic properties at high temperatures, XVIIIth International Congress, Pure and Applied Chemistry", Montreal, Canada, August 6-12, 1961.

91. L. Brewer, G. R. Somayazula and E. Brackett, Chem. Rev., 63, 111 (1963).

92. K. K. Kelley - Bulletin 584, U.S.Department of the Interior, Bureau of Mines (1960).

93. K. K. Kelley and E. G. King, - Bulletin 592, U.S. Department of Interior, Bureau of Mines (1961).

94. L. Brewer - Chemistry and Metallurgy of Miscellaneous Materials - University Micro films, edited by L. L. Quill, McGraw Hill Book Co. Inc., 1950, New York, Toronto, London.

95. Private letter from Dr. W. S. Horton, Chief High Temp. Chemistry Section, U.S. Deptt. of Commerce, N.B.S., Washington DC.

96. H. Schäfer, F. E. Berhard Wittig and W. G. Wilborn, Z.anorg.u.allgem.chem., 297, 48 (1958).

97. W. Fischer and R. Gwehr, Z.anorg.u.allgem.chem., 209, 17 (1932).

98. M. Farber and A. Blauer, Trans. Far. Soc., 58,2090(1962).

99. M. Farber and Petersen, Trans. Far. Soc., 59, 836 (1963)

100. M. A. Greenbaum, J. A. Blauer, M. R. Arshadi and M. Farber, Trans.Far. Soc., 60, 501, 1592-7 (1964).

101. A. Semenkovitch, Zh. Prikl. Khim., 33 (1960).
J. Appl. Chem. USSR, 33, 557 (1960).

102. L. M. Lenev and I. A. Novokhatskii, Russ. Jou. Inorg. Chem., 10, 1307 (1965).

103. Standard X-ray Diffraction Powder Patterns - N.B.S. Circular No: 539, Vol.I(47), Vol.9(42)(1956).

104. "JANAF" Thermochemical Tables - Revised ed. The Dow Chemical Co., Midland, Mich., 1964 and 1965.

105. S. Senderoff, G. W. Mellors, R. I. Bretz, Annal. New York Acad. Sciences, 79, 878 (1959).

106. L. Yamarkouski, E. Ya Pesina and R. I. Smirnova, Zh. Prikl. Khim., 38, 411 (1965).

107. M. Atchayya, B. Seshagiri Rao and V.V. Dadape, Ind. Jou. Chem., 48, 370-71 (1966).

108. G. I. Novikov and A. K. Baev, Russ. Jou. Inorg. Chem., 7, 694 (1962).

109. S. J. Yosim and E. B. Luchsinger, Annal. New York. Acad. Sci., 79, 1079 (1959).

110. V.V. Zhukovetskii, Trudy Severo Kav Kaz. Gornomet. INST., 15, 210-31 (1957).

111. H. Balduin, Monatshe Fur Chem., 88, 1038 (1957).

112. B. J. Chai, H. C. Ko, M.A. Greenbaum and M. Farber, J. Phys. Chem., 71, 3331-36 (1967).

113. F. Irman, Helv. Chim. Acta. 33, 1449 (1950).

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