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STUDIES

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EQUILIBRIUM STUDIES
INVOLVING LIGHT METALS
AND THEIR COMPOUNDS AT
HIGH TEMPERATURES

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By

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A Thesis Submitted to
The University of Poona

for

The Degree of Doctor of Philosophy

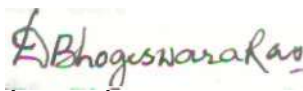
ACKNOWLEDGEMENT

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The author is indebted to Dr. T. B. Douglas of the National Bureau of Standards for making available the thermal functions for $\text{BeO} : \text{Al}_2\text{O}_3$ and Dr. W. S. Horton, Chief of the High Temperature Chemistry Section, NBS, Washington, DC, USA, for useful suggestions and helpful discussions. He is also thankful to the NBS authorities for the permission to utilize the equipment in the PL-480 scheme on "The chemical and thermodynamic properties of refractory materials at high temperatures" at the National Chemical Laboratory, Poona, India.

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(D. Bhogeswara Rao)

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CHAPTER - I

INTRODUCTION

developing modern industries, and other projects

CHAPTER - I

INTRODUCTION

1.1. GENERAL

Research in high temperature chemistry has been accelerated considerably in the course of the last two decades. In this period considerable advancement has been made in the study of thermodynamics and kinetics of high temperature processes. Prior to that, high temperature chemistry was restricted to 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 industries, has given proper impetus for the study of high temperature processes. Flames, arcs and discharges, plasma jets, shock waves and exploding wires, are available for the production of temperatures in the range of $3500 - 100,000^{\circ}\text{K}$. Temperatures as high as $10^6 - 10^8\text{K}^{\circ}$ are now produced by nuclear fusion.

1.2. The attainment of high temperatures by chemical means involves the production of large amounts of heat and formation of stable gaseous products. Temperatures upto 6000°K can be obtained by chemical reactions¹. At these temperatures large concentrations of atoms and molecules may be obtained in electronic states other than ground states.

Thus the existence of various kinds of odd molecules electron deficient and also with non-localized bonding etc. are common at high temperatures. In extreme cases ions and bare nuclei are the main species. High temperature chemistry therefore refers to the chemistry of systems at sufficiently high temperatures, where the oxidation states, compounds and general chemical behaviour differ appreciably from those at room temperatures². Previously, optical spectra had been quite useful in identifying high temperature gaseous species. The use of the mass spectrometer for the study of high temperature gaseous products has yielded spectacular results in the past few years. The combination of optical and mass spectrometric methods greatly accelerated the elucidation of high temperature gaseous systems. 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 , Ga_2C_2 , $Be(OH)_2$, $Si(OH)_4$, 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 and CF_2 , etc.

1.2. IMPORTANT HIGH TEMPERATURE REACTIONS

With the advent of these developments new chemicals have been synthesised, which are useful materials in industries like chemical, automobile, aviation and in rockets, satellites,

and nuclear reactors. The production of industrial graphite from carbon, preparation of ceramics and ceramets such as carbides, borides, silicides, nitrides, etc. new fuels and propellant ingredients for rockets, preparation of fluorocarbons, single crystals, HCN from methane and ammonia, cracking of hydrocarbons and nitrogen fixation, are a few achievements of chemical reactions at high temperatures.

A number of stable species are yet to be identified in important systems. Possibilities for the production of new and important materials depend directly on the existence of unusual species, which can act as intermediates at high temperatures. These, a type of free radicals which are very reactive and industrially useful, have been obtained only through the application of high temperatures. For a complete characterization of high temperature chemical reactions the determination of the stabilities and chemical nature of high temperature gaseous products is very important.

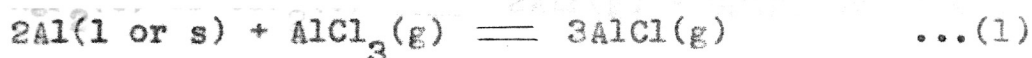
1.3. CHEMICAL TRANSPORT REACTIONS

There are two ways of obtaining such important useful intermediates (a) by directly heating the compounds and elements to higher and higher temperatures until they give unusual gaseous species with different oxidation states

e.g. Al_2O_3 , ZrO_2 , TiO_2 , C_2 , C_3 , CN , Ba_2O , Ba_2O_2 , BeO , B_2O_2 , etc. and (b) the unusual gaseous species will also result from vapour-condensed phase or solid-liquid interactions, e.g. metal-metal halide systems, metal-metal sulphide systems, etc. The species are Al_2O , AlCl , AlF , BeCl , BF , $(\text{BOF})_3$, AlOCl , AlS , etc.

1.3.1. Definition of chemical transport reaction

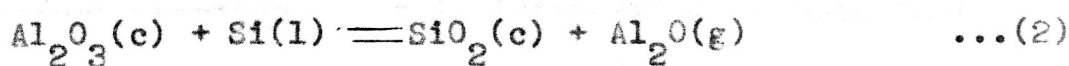
When aluminium chloride vapour is passed over heated aluminium bearing material the equilibrium approached in the hot zone is



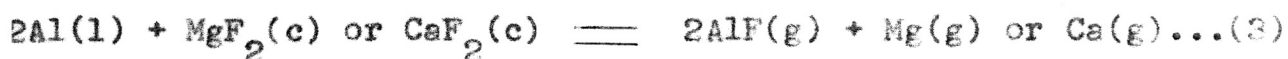
and reverts on cooling to produce pure aluminium and normal halide. Thus the production of aluminium through the formation of aluminium monochloride was described by Gross³ as catalytic distillation or subhalide distillation. The formation of subhalide helps to overcome the high energy barrier for the distillation of metal, by promoting it to vapour phase. Schäfer⁴ in 1962 named this type of heterogeneous reactions as chemical transport reactions. This term, however, has wide application. He defined chemical transport 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. $\text{Al}_2\text{O}(\text{g})$ ⁵.



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 subhalide⁶:



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

Thus the chemical transport reaction 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.

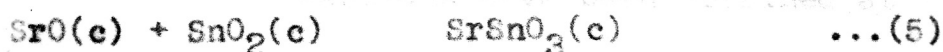
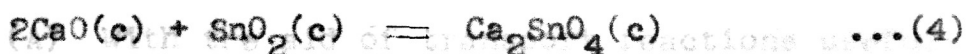
1.4. IMPORTANCE OF CHEMICAL TRANSPORT REACTIONS

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

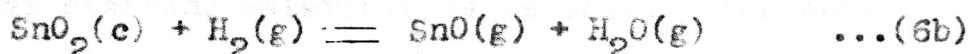
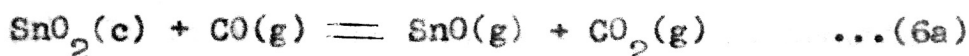
to produce and refine metals, in the preparation of alloys, synthesis of new compounds, etc.

1.4.1. In solid state reactions

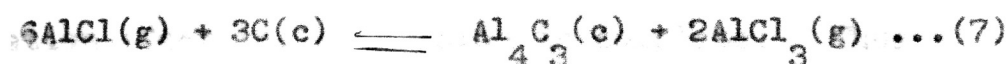
Reaction between the starting solid materials can be enhanced when solid substances are joined together by a transport reaction. It is interesting to note that in a whole series of reactions with solids as starting materials, it has been shown that a liquid or gas phase is involved as a reaction promoter⁷, 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}



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



One of the most important and recent chemical transport reactions is the formation of aluminium carbide by the action of aluminium monochloride on carbon¹¹.



Heim¹¹ 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, etc. The formation of magnesium aluminate (MgAl_2O_4) through aluminium monochloride and MgO has been described 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 only at 1700 to 1800°C¹⁴ whereas according to equation (7) the formation takes place at much lower temperatures 900-1300°C¹¹.

(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 higher purity.

(D) The components of the reaction need not be mixed since one of them can be transported to the other^{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 crystals¹⁵. The identification and chemical transport of the gaseous species $\text{Si}(\text{OH})_4$ ¹⁶, $\text{Be}(\text{OH})_2$ ¹⁷ and the hydroxides of Zn, W¹⁸ and B¹⁹ provided methods for the removal of trace impurities²⁰.

1.4.4. Use of chemical transport reactions in metallurgy

Out of the innumerable applications of these reactions a few very important ones are given below:

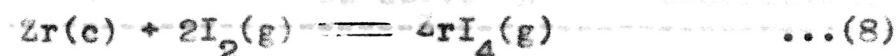
(A) Mond-Longer process

This process, which involves the reversibility of the reaction, was used for refining nickel²¹. Finely powdered crude nickel when treated with carbon monoxide at 50° and

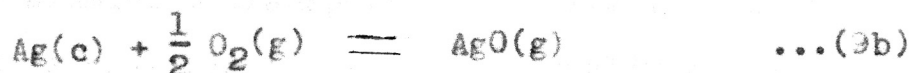
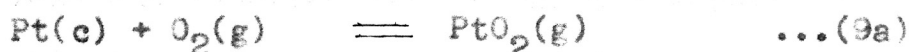
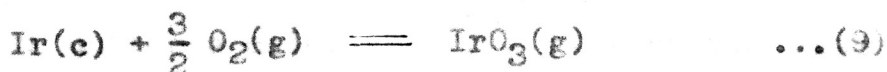
atmospheric pressure evaporates as nickel carbonyl, Ni(CO)_4 . This gas when led into a decomposition tower decomposes to pure granular nickel.

(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 Arkel²² is very useful for the purification of metals. In this the crude metal is vaporized as iodide and is decomposed on a hot wire²³



(D) Under suitable conditions metals like iridium²⁴, platinum²⁵ and silver²⁶ can be removed and pure crystals can be grown by transporting them through a stream of oxygen:



It is also possible to transport ruthenium, rhodium and palladium in chlorine atmosphere²⁷⁻²⁹.

1.5. IMPORTANCE OF THE MONOCHLORIDE OF ALUMINIUM

The reaction (1) which was mentioned earlier has a wide application for the production and refining of aluminium. The purity of the metal produced³⁰ reveals the importance of this method (table 1).

Table 1

Purity of aluminium metal obtained
by reaction (1)³⁰

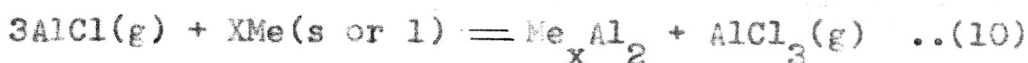
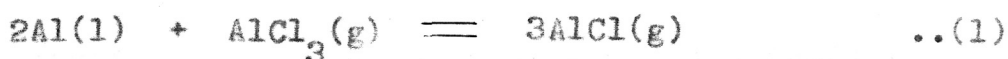
Impurity	In crude metal %	Metal obtained as above %	Purification coefficient %
Cu	3.36	< 0.05	< 0.015
Si	1.74	< 0.04	< 0.023
Fe	1.28	< 0.06	< 0.05
Mn	0.35	< 0.05	< 0.14

Many patents claim the production of pure aluminium through the formation of unstable chloride³⁰⁻³⁶. Gross did pioneering work in this field and reported many times the separation effects in the aluminium transport via AlCl(g) . According to Gross³⁷, it is possible to prepare thermally an Al(Si,Fe) alloy directly from its ore and the alloy can be decomposed by the removal of aluminium through a transport process.

Nowotny, Balduin and Piffel³⁸ were able to transport aluminium almost completely out of an Al-Ti alloy in a stream of $H_2 - AlCl_3$ at 1400° via $AlCl(g)$. Al-Ti alloy was obtained alumino-thermally from TiO_2 . This is a new method to prepare titanium.

In recent years the importance of the monochloride has been realized³⁹ and the development of the process will provide new ways for the technical recovery of aluminium⁴⁰.

Apart from its use in refining aluminium, the monochloride is very useful for the preparation of important compounds¹¹. The formation of alloys are also possible by utilizing this highly reactive unstable species



1.6. AIM AND OBJECTIVE OF THE PRESENT WORK

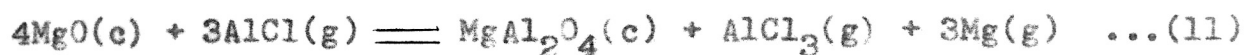
Due to the highly reactive nature of the unstable subhalide vapour ($AlCl$) several interesting reactions are possible in which it reacts with oxides of Mg, Be, Al, etc. The present work aims at studying the following reactions:

(A) The equilibrium of the following reaction:



at high temperatures to determine the heat of formation of the reactive and unstable $AlCl(g)$.

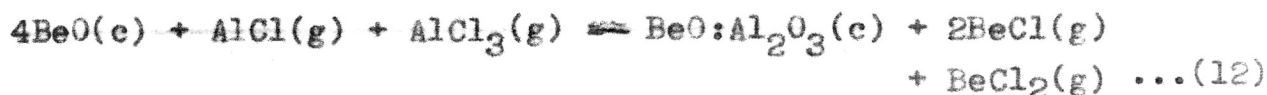
(B) The reaction between $\text{AlCl}(\text{g})$ and $\text{MgO}(\text{c})$



In order to elucidate the reaction mechanism it is necessary to carry out equilibrium measurements together with the quantitative analysis of the reaction products.

(C) The reaction of $\text{AlCl}(\text{g})$ with $\text{MgAl}_2\text{O}_4(\text{c})$ at temperatures 1300-1400°K employing a synthetic sample of $\text{MgAl}_2\text{O}_4(\text{c})$. Knowing the reactivity of $\text{AlCl}(\text{g})$ with $\text{MgAl}_2\text{O}_4(\text{c})$, the spinel can be prepared by reducing $\text{MgO}(\text{c})$ aluminothermally and transporting excess aluminium metal via $\text{AlCl}(\text{g})$.

(D) The reaction between $\text{AlCl}(\text{g})$ and $\text{BeO}(\text{c})$ in order to establish the reaction scheme:



Beryllium, like aluminium, forms subhalides and is more electronegative than aluminium and also high up in the aqueous activity series. It is also to be noted that the literature values for the heat of formation of $\text{BeCl}(\text{g})$ are widely varying and hence there is a need to determine the thermodynamic properties of $\text{BeCl}(\text{g})$.

or differentiation
CHAPTER - 2

dynamic quantities and
THERMODYNAMIC CONSIDERATIONS

CHAPTER - 2

THERMODYNAMIC CONSIDERATIONS

2.1. THERMODYNAMIC STUDY

Thermodynamic relations are of great help in describing high temperature reactions. These relations are possible when the thermodynamic quantities are known accurately for all the compounds. Therefore, the evaluation and correlation of thermodynamic data are important aspects of chemical thermodynamics. Results of different methods or different investigations must be used for the critical selection of values for a substance. A knowledge of thermodynamic quantities like heat of formation, enthalpy, entropy and free energy as functions of temperature is finding ever increasing use to 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 accumulation and storage of data are therefore quite rewarding.

Thermodynamic study of high temperature reactions is based on the measurement of the equilibrium pressures of the reaction. The study of vaporization process or the equilibrium of reaction helps to establish the nature and

energetics of chemical binding in the gaseous state.

As is stated by Gilles⁴¹ the study of high temperature reaction should be on the following lines:

- (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 temperatures. The first two were given by Brewer⁴² and the third by Searcy⁴³. As these generalizations are of great use in the present work, the statements are only quoted here. A detailed discussion has been given in the literature⁴⁴.

- (A) The higher the temperature of a vapour-solid or vapour-liquid equilibrium, the more nearly equal will be the partial pressures of the various vapour species.
- (B) A gas will only react endothermically with a solid to produce a significant yield of a reaction product, if the reaction produces at least as many moles of gas as are consumed in the reaction.

(C) All equilibrium reactions that yield more products when the temperature is increased must be endothermic and must occur with an increase in entropy. This statement is also 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 were described in detail by Margrave⁴⁵.

namely,

2.3.1. Equilibrium pressures by direct measurements

Because of the high temperatures involved and the experimental difficulties arising from the very active nature of aluminium monochloride, it is not possible to measure the pressures of reaction (1) by direct methods; viz. manometers, sickle gauges, boiling point observations, dew point method and vapour densities. The unstable monohalide reacts with the material of which any manometer etc. might be constructed⁴⁶.

2.3.2. Vapour pressures by indirect measurements

For measuring vapour pressures less than 10^{-3} atms. the techniques employed are Langmuir, Knudsen effusion, torsion effusion, molecular flow effusion, optical spectroscopy and mass spectrometry. For measuring pressures greater

than 10^{-3} atms. in a satisfactory way, flow or transpiration method is the only one which is simple and very useful.

2.3.3. Langmuir free evaporation

This method is not applicable for the study of equilibrium pressures of a heterogeneous reaction (1).

2.3.4. The Knudsen effusion method

A large number of thermodynamic data at high temperatures has been obtained with the help of the Knudsen effusion method. However, many of its aspects namely, the correction to be applied for 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 and reported in the literature⁴⁸⁻⁵¹. Apart from the above, 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 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 on opposite sides displaced in opposite directions from the centre. Vapour effusing through the holes causes a torque to be exerted on the cell and rotational displacement of the cell 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 vapour. Searcy and Freeman^{51a,51} obtained low values for tin and germanium when compared to the mass spectrometric results. The scope of this method and its limitations are discussed in detail by Gilles⁴¹.

2.3.6. Molecular flow effusion method

The molecular flow effusion method was developed by Farber⁵² in 1962. This method involves an impinging gas at the temperature of the reaction striking the reacting material at pressures allowing free molecular flow. The concentration of the molecular constituent is determined by the equilibrium constant, employing the Knudsen equation:

$$n = \frac{P}{(2 \pi m K t)^{1/2}} \quad \dots(13)$$

n = number of moles striking the surface.

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2.3.7. Optical spectroscopy

In the past, optical spectroscopy has been one of the most important techniques to determine structure and thermodynamic properties of the gases produced in the chemical reactions at high temperatures. From optical spectra it is possible to determine the molecular configuration, electronic, vibrational and rotational energy levels. Spectroscopy thus provides data for computation of thermodynamic properties by statistical methods. However, this method has limited scope in finding out correct dissociation energies of some compounds even though the data is sufficient in making a satisfactory estimate^{of entropy}. For example the dissociation energy of AlCl(g) was found too low ($D_0^0 = 3.1 \text{ ev}$)⁵³. This was found to be due to the unreliability in the Birge-Sponer extrapolations for molecules of the metals which have low ionization potentials where the ionic bonding forces are important. In this case the unambiguous identification is not possible⁵⁴.

The value of dissociation energy for AlC.D_0^0 (AlC) = $1.6 \pm 0.2 \text{ ev}$ obtained by Zeeman⁵⁵ from the analysis of emission spectra is far too low. The anharmonicity coefficients are difficult to determine by spectrographic methods for complex molecules.

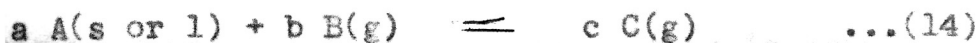
2.3.8. Mass spectrometer

Mass spectrometer is one of the most important tools employed in the high temperature chemistry. The method consists of the ionization of the high temperature vapour by electrons and identification of the resulting ions. Inghram and Drowart⁵⁶ have given an excellent discussion of mass spectrometry and its applications to high temperature chemistry.

2.4. FLOW, TRANSPIRATION OR TRANSPORTATION METHOD

Though this dynamic method (transpiration) was reviewed by many authors^{4,27,45,57-60} yet complete details are still lacking. A full description, therefore, will not be out of place here.

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. In such cases the material will be carried away by a stream of an inert gas which is passed over or bubbled through the evaporating sample at constant temperature and applied pressure. On the other hand, in the vapor-condensed phase equilibria, the solid or liquid which will have no appreciable vapour pressure at that temperature can be transported by the formation of vapour phase reaction products. In this case the transport medium is the vapour B



Thus the transport of solid substance presupposes the motion of a gas. In the above reaction, if the transporting medium has a 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 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 extremely simple flow techniques.

In the case of this flow technique all the gaseous components migrate with the same speed, consequently the ratios are simpler than the other methods. The gases are assumed ideal and the carrier gas must be saturated with the vapours of the material under study, or the products of reaction. Then by Dalton's law, the partial pressure of each component P_1 is proportional to the number of moles of the gas n_1 . Thus for an inert gas flow 'f' and one vapour species

$$\frac{P_v}{P_T} = \frac{P_v}{P_v + P_f} = \frac{n_v}{n_v + n_f} \quad \dots(15)$$

Now n_v can be determined from the weight loss of a sample from the amount of solid deposited on the cold finger or by the analyses of the products trapped in a flow system.

If the molecular weight of the vapour species is known or assumed, n_f from the flow rate calibration experiments, P_T the pressure at which the system is in equilibrium, P_v can be determined.

2.4.1. Equilibrium in transportation study

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

- (A) All the reagents participating in the reaction must be at the equilibrium temperature. This will be facilitated by preheating the gases before they enter into the reaction zone. In the case of vapour-liquid or vapour-solid equilibria, the transport medium with or without diluent gas must be preheated up to the equilibrium temperature before it reacts with solid or liquid and equilibrates with it.
- (B) The pressure of the equilibrium zone must be the same as that of the entire flow system. Temperature and pressure gradients cause the reverse reaction to occur i.e. the reformation of solid reactants. The apparatus should be so chosen as to avoid the above difficulties⁶¹.
- (C) The reaction zone must attain equilibrium and remain undisturbed during the transportation period. Change of flow rate or very high thermal gradients causes the reaction

to shift in such a way that the transport of material observed will differ largely from that of the normal experiments.

(D) Some unwanted reactions due to imperfect gas flow may decrease the surface area of solid or liquid under study, so that the reaction rate will deviate far from equilibrium, e.g. in the case of Al-AlCl₃ system (Chapter 3), if the carrier gas argon contains appreciable amounts of O₂, N₂ and water vapour, they will react with aluminium or aluminium trichloride or monohalide with the formation of alumina and aluminium nitride coatings on the sample, hindering further reaction, thus giving much lower transport of aluminium. The carrier gas has therefore to be perfectly dry.

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

(F) Flow rate should be measured accurately.

(G) Side reactions between sample and container or flow gas or product with the reaction tube should be avoided. Very few refractory materials are suitable for molten metals. For equilibrium measurements it is therefore necessary to test these materials for which the free energy change for simple reduction by the liquid metal has a large positive value. Brewer⁶² has illustrated the use of thermodynamics in the search for a suitable container for melting titanium. If an

extensive contamination or reaction occurs the material should be brought to equilibrium with liquid metal or reactive species, so that it is saturated with respect to solution, either of the metal itself or of the products of the reaction between metal and refractory material; this will minimise the attack or container will be passivated. Attack by melt normally involves the penetration through a solid container by intergranular solution process and the rate of this attack depends primarily on kinetic factors e.g. diffusion and viscosity.

2.4.2. Saturation of flow or carrier gas

The flow 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 dependant on the construction of the apparatus. The flow gas has to ensure equilibrium with solid or liquid. According to Schäfer⁴ "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 few centimeters. The gas passes over the solid in an ideal case, equilibrates with it completely. For the fore-mentioned tube diameter and for the temperatures of solid above 500°C, gas flows

from 2-10 litres per hour (20°C , 1 atm.) have usually proved to be satisfactory. When the reaction between gas phase and solid substance proceeds very slowly, or when one is forced to use slow gas flow rates larger amounts of solid and longer reaction zones are recommended".

The high flow rates can be used if the chemical reaction attains equilibrium quite rapidly. In the high temperature systems 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, large 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 substances have velocity coefficients which are close to 1, i.e. their 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, low velocity coefficients will be ^{observed} ~~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, there-

fore, 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 made 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 $\frac{nv}{nc}$ vs n_f (← equation 15) should approach ∞ at $n_f = 0$ and shows a plateau region for n_f values where saturation is complete. For unsaturated flow the plot will not level off. This feature has been discussed by Lepore and Van Wazer⁵⁸. 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 mixture⁵⁹.

However, it can be shown that at sufficiently high flow rates, diffusion effects become negligible. Diffusion occurs when the rate of flow is too slow and the apparent pressures will be too high. Merten^{59,27} derived the equation:

$$P = \frac{m}{tv} \frac{RT}{M} \left[1 - \exp \left(- \frac{v l}{DA} \right) \right] \quad \dots(16)$$

in which P is the pressure, R and M are gas constant, temperature $^{\circ}K$ 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 unimportant and the pressure assumes the usual value

$$P = \left(\frac{m}{tv} \right) \left(\frac{RT}{M} \right) \quad \dots (17)$$

but at small values of v the diffusion coefficient is given by:

$$P = \frac{m}{t} \frac{RT}{M} \left[\left(\frac{DA}{l} \right) + \frac{v}{2} \right]^{-1} \quad \dots (18)$$

He also pointed out that the equation may be used to obtain not only the pressure but also diffusion coefficient in favourable instances. Ackerman et.al.⁶³ have confirmed the validity of this equation. According to Merten^{59,27} reliable pressure can be calculated if experimental determinations are available at two significantly different flow rates for which saturation has been reached.

2.4.3. Advantages of transpiration method

The significance of this experimental technique is brought out in the case of silicon transport in the chloride system⁶⁴⁻⁶⁶. Schäfer⁶⁴ by using the flow method transported considerable amount of SiCl_2 to a cold zone without disproportionation. At lower temperatures it combined with SiCl_4 to form Si_2Cl_6 , Si_3Cl_8 , etc.⁶⁶.

Another important feature of this method is the ease with which corrosive, unstable vapour species are handled

successfully and in a useful way.

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, quenching methods and improved analytical techniques may help to solve this 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: (14) the:

$$P = \frac{nRT}{V_T} \quad \dots(19)$$

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

$$P = \frac{nRT_r}{V_r} \quad \dots (20)$$

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

$$P_C = \frac{c}{a} \frac{n_A RT_r}{V_r} \quad \text{or} \quad \frac{c}{a} \frac{\Delta W RT_r}{M V_r} \quad \dots (21)$$

$$P_{B \text{ unreacted}} = \left(n_B - \frac{b}{a} n_A \right) \frac{RT_r}{V_r} \quad \dots (22)$$

OR

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

$$\text{The equilibrium constant} \quad K = \frac{P_C^c}{P_B^b} \quad \dots (23)$$

2.5. THE EQUILIBRIUM CONSTANT

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

$$\partial F = 0 \quad \dots (24)$$

i.e. that the free energy remains unchanged in any infinitesimal process occurring 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 (14) the:

$$\Delta F^0 = - RT \ln K \quad \dots (25)$$

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

$$d \left(\frac{\Delta F^\circ}{T} \right) = - \frac{\Delta H^\circ}{T^2} dT = \Delta H^\circ d \left(\frac{1}{T} \right) \quad \dots(26)$$

Substituting equation (25) for F° in equation 26, one obtains the Vant Hoff's equation:

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2} \quad \dots(27)$$

OR

$$\frac{d(R \ln K)}{d \left(\frac{1}{T} \right)} = \frac{4.5758 d \log K}{d \left(\frac{1}{T} \right)} = -\Delta H^\circ \quad \dots$$

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^0 for the process is constant over the temperature range investigated. From Kirchoff's equation:

$$\left[\frac{\partial(\Delta H^0)}{\partial T} \right]_P = \Delta C_p^0 \quad \dots(28)$$

Therefore, if the heat capacity equations are available for the reactants and products an improved procedure is possible^{67,68}. The treatment includes the use of the following equations:

$$\frac{\Delta F}{T} = -R \ln K = \frac{\Delta H^0_I}{T} - \Delta a \ln T - \frac{1}{2} bT - \frac{1}{2} \Delta cT^{-2} + I \quad \dots(29)$$

where I is constant.

$$\frac{\Delta H^0}{T} + I = \Sigma = -R \ln K + \Delta a \ln T = \frac{1}{2} \Delta bT + \frac{1}{2} \Delta cT^{-2} \quad \dots(30)$$

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 Σ against $1/T$ gives a straight line with a slope ΔH^0_I . From the value of H^0_I one can obtain ΔH^0_T at any temperature range for which the heat capacity equations are applicable.

If the contribution of ΔC^0_P 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 Σ 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: $\left(\frac{F_T^O - H_T^O}{T} \text{ ref} \right)$ 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 Margrave⁶⁹.

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

$$F_T^O = H_T^O - T S_T^O \quad \dots(31)$$

one obtains

$$\frac{F_T^O - H_T^O}{T} = -S_T^O \quad \dots(32)$$

by adding the quantity $\left(\frac{H_T^O - H_T^O \text{ ref}}{T} \right)$ (the heat content

above a reference temperature usually 0°K or 298°K , divided by T) to both sides of the equation one gets

$$\frac{F_T^O - H_T^O}{T} \text{ ref} = -S_T^O + \frac{H_T^O - H_T^O \text{ ref}}{T} \quad \dots (33)$$

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

$$\frac{F_T^O - H_{298}^O}{T} = \frac{F_T^O - H_O^O}{T} - \frac{H_{298}^O - H_O^O}{T} \quad \dots(34)$$

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:

$$S_T^O = \int_{T_0}^{T_1} C_p d\ln T + \frac{\Delta H_{Tr}}{T_1} + \int_{T_1}^{T_2} C_p d\ln T + \int_{T_1}^T C_p d\ln T \quad \dots(35)$$

and

$$\frac{H_T^O - H_{T_{ref}}^O}{T} = \frac{1}{T} \left[\int_{T_{ref}}^{T_1} C_p dT + \Delta H_{Tr} + \int_{T_1}^{T_2} C_p dT + \int_{T_1}^T C_p dT \right] \quad \dots(36)$$

In the case of gaseous molecules it is possible to determine the value of "fef" directly through the use of statistical thermodynamics and spectroscopic data⁷⁰.

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

$$\Delta fef = (fef)_{\text{products}} - (fef)_{\text{reactants}} \quad \dots(37)$$

After collection of the terms and consolidation one obtains:

$$\Delta fef = \frac{\Delta F_T^O}{T} - \frac{\Delta H_T^O \text{ ref}}{T} \quad \dots(38)$$

$$\Delta H_T^O \text{ ref} = T \left(\frac{\Delta F_T^O}{T} - \Delta \frac{F_T^O - H_T^O \text{ ref}}{T} \right) \quad \dots(39)$$

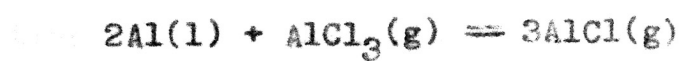
Substituting equation 25 in equation 39, the equation can be written as:

$$\Delta H_{T \text{ ref}}^{\circ} = T (-R \ln K - \Delta'_{\text{fef}}) \quad \dots(40)$$

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 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.

CHAPTER - 3

EQUILIBRIUM STUDIES OF THE REACTION



CHAPTER - 3

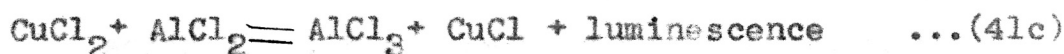
EQUILIBRIUM STUDY OF THE REACTION $2\text{Al}(l) + \text{AlCl}_3(g) \rightleftharpoons 3\text{AlCl}(g)$ 3.1. INTRODUCTION

The importance of aluminium monochloride (AlCl) in the metallurgy of aluminium and in the synthesis of some important compounds has been discussed earlier (Chapter 1.5). It has also been mentioned (Chapter 2.1.) that how the equilibrium studies and thermodynamics help in characterizing the species at high temperatures and in understanding its stability and chemical reactivity. This chapter describes the experimental work on the study of the equilibrium of the above reaction and the evaluation of the thermodynamic data employing the transpiration technique.

3.1.1. Evidence for the existence of $\text{AlCl}(g)$

Jevons^{71,72} was the first to detect and identify the spectrum of aluminium monochloride during the study of the spectra of silicon tetrachloride. Similar spectrum was also observed when hydrogen chloride was subjected to a high voltage discharge between aluminium electrodes.

Frommer and Polanyi⁷³ observed a luminescence ascribable to cuprous chloride bands when chlorine reacted with aluminium in the presence of copper. They thought the cause for luminescence was the formation of aluminium dichloride which should have strong reducing property. Their scheme can be written as:



In addition to the above evidence the work of Bhaduri and Fowler⁷⁴, Holst⁷⁵, Miescher⁷⁶ and Mohanti⁷⁷ gave an added confirmation to the existence of aluminium monochloride in the vapour phase.

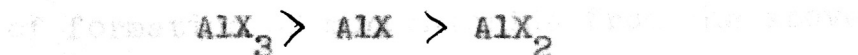
3.1.2. The role of spectroscopic data

The spectroscopic data were sufficient in making a satisfactory estimate of the entropy of $\text{AlCl}(\text{g})$ but the dissociation energy was found to be too low. This was due to the unreliability inherent in the Birge-Sponer extrapolations (Chapter 2.3.7).

3.1.3. Theoretical study

Aluminium has got two s electrons and one p electron beyond the inert gas configuration. Thus the lower valency results from the loss of p electron. The fairly large difference between the first and second ionization potentials can also be the reason for the existence of monovalent aluminium. Using the Born-Haber cycle, Irman⁷⁸ has calculated the energies of formation of both gaseous and solid aluminium (I and II) halides. Though the unreliability in these values is high, they help to determine the relative stabilities of aluminium sub-halides. The following are his conclusions:

(A) The order of stability is given as:



(B) Solid AlX is only slightly less stable than solid AlX₃, the degree of instability is the same for all halides.

(C) The stability of gaseous AlX relative to gaseous AlX₃ decreases in the order of fluoride, chloride, bromide, iodide.

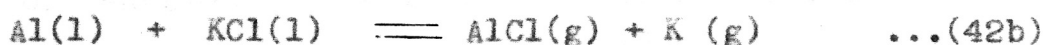
(D) Gaseous AlX is stable at higher temperatures.

3.1.4. Chemical evidence

The chemical evidence for the aluminium subchloride was provided by Klemm, Voss and Geirsberger⁷⁹ and Gross and his co-workers³². Particularly, the work of Klemm et.al.⁷⁹ in this connection was very interesting.

3.1.5. The equilibrium study of the reaction (1)

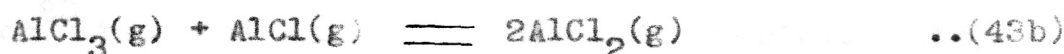
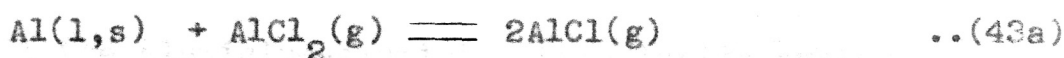
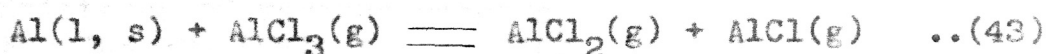
Since the dissociation energies estimated by spectroscopic data are grossly in error the resultant heat of formation will not be reliable. It is therefore necessary to determine the heat of formation by the study of the equilibrium. Gross ⁴⁶et.al. have reported their results of the study of the equilibrium reaction between Al(l) and AlCl₃(g). The following equilibria have also been investigated by these authors:



A value of - 11.58 Kcal. mole⁻¹ was deduced by them for the heat of formation of monochloride from the above equilibria. The ΔH_{f298} values of AlCl(g) from the above reactions did not correspond well with that obtained from the reaction



The observed difference of more than 4 Kcal. in the free energy of the reaction has been attributed to the unreliability of thermochemical data for AlCl₃(g) and to the fact that equilibrium might not have reached during the experiment. In reaction (1) the matter appears to be complicated by the possibility of formation of AlCl₂(g). Experimental values of Heimgartner⁸⁰ disagree with the calculated ones, consequently the equilibrium reaction (1) was neglected and the following reactions were proposed:



AlCl₂ being considered as the main species. However, there is no evidence in the literature about the stability of AlCl₂(g) species at high temperatures. Irman's theoretical values also reveal that the AlCl₂(g) is relatively less stable when compared to AlCl(g) at high temperatures.

Russel et.al.⁸¹ have measured the equilibrium constant of reaction (1) at 1400^o K and obtained a third law value for ΔH_{f298} of -12.18 Kcal.mole⁻¹. The study of this

reaction between 950-1200° by Semenovitch⁸² gave a second law heat of reaction at 298°K of 77.98 Kcal. mole⁻¹ which led to a value of $\Delta H_{f298} = -19.20$ K cal. mole⁻¹. The ΔH_{f0}° value of Weiss⁸³ was -17. Kcal. mole⁻¹.

Foster et.al.⁸⁴ and Heise and Wieland⁸⁵ have calculated from spectrographic measurements the ΔH_{f0}° of AlCl(g) giving the values -13.8 and -10.5 ± 2 Kcal.mole⁻¹ respectively. Borrow⁸⁶ calculated the dissociation energy of AlCl(g) $D_{298}^{\circ} = 117.6$ from thermochemical data which gave value -11.1 for the ΔH_{f298} of AlCl(g). Thus the values reported in the literature for the ΔH_{f298} of AlCl(g) vary from -11 to -20 Kcal. mole⁻¹. The values are summarized in Table II.

3.1.6. Existence of various gaseous species and their stabilities

In the aluminium-aluminium trichloride system, Heimgartner⁸⁰ reported AlCl₂(g) as the main species. The importance of the species at high temperatures will depend upon their relative stabilities. The stability of different species at high temperatures can be explained on their relative bond strengths. The dissociation profile at high temperatures of a gas of the type MX_n will depend upon the relative bond strengths in the dissociation species MX_{n-1}, MX_{n-2} and MX. Several fluoride and oxide species were studied by Siegel⁸⁷. The bond energy term is a quantity which when summed over all the bonds, gives the heat of formation of the molecule from

Table - II

Literature values for the heat of formation of $\text{AlCl}(\text{g})$

Chemical reaction	$\Delta H_f^\circ \text{AlCl} \text{ Kcal. mole}^{-1}$	Reference
$\text{AlCl}(\text{g}) \rightleftharpoons \text{Al}(\text{g}) + \text{Cl}(\text{g})$	$= + 34.5$	Herzberg 53
$\text{AlCl}(\text{g}) \rightleftharpoons \text{Al}(\text{g}) + \text{Cl}(\text{g})$	$= - 11.6$	Caydon 54
$\text{Al}(\text{l}) + \text{NaCl}(\text{c}) \rightleftharpoons \text{AlCl}(\text{g}) + \text{Na}(\text{g})$	$= - 11.35$	Gross et al. 46
$\text{Al}(\text{l}) + \text{NaCl}(\text{l}) \rightleftharpoons \text{AlCl}(\text{g}) + \text{Na}(\text{g})$	$= - 12.12$	Hei 35 -do-
$\text{Al}(\text{l}) + \text{KCl}(\text{l}) \rightleftharpoons \text{AlCl}(\text{g}) + \text{K}(\text{g})$	$= - 11.58$	-do-
$2\text{Al}(\text{l}) + \text{AlCl}_3(\text{g}) \rightleftharpoons 3\text{AlCl}(\text{g})$	$= - 10.39$	-do-
Theoretical		Irman 78
	$\Delta H_f^\circ \text{AlCl} = - 5$	-do-
	$\Delta H_f^\circ \text{AlCl}_2 = - 30$	Heimgartner 80
$2\text{Al}(\text{l}) + \text{AlCl}_3(\text{g}) \rightleftharpoons 3\text{AlCl}(\text{g})$	$\Delta H_f^\circ \text{AlCl} = - 10.28$	-do-
	$\Delta H_f^\circ \text{AlCl}_2 = - 76$	Russel et al. 81
-do-	$\Delta H_f^\circ \text{AlCl} = - 12.18$	Semenkovitch 82
-do-	$\Delta H_f^\circ \text{AlCl} = - 13.6$	-do-
-do-	$\Delta H_f^\circ \text{AlCl} = - 19 \text{ (2nd law)}$	Weiss 83

Table - II (cont...)

Chemical reaction	ΔH_f AlCl Kcal. mole ⁻¹	Reference
$2Al(l) + AlCl_3(g) \rightleftharpoons$	$3AlCl(g) \Delta H_{fO}^\circ = - 13.8$	⁸⁴ Foster et.al.
-do-	-do- $\Delta H_{fO}^\circ = - 10.5$	Heise and ⁸⁵ Wieland
-do-	-do- $\Delta H_{fO}^\circ = - 16.4$	Miescher ⁷⁶
$AlCl(g) \rightleftharpoons Al(g) + Cl(g)$	$\Delta H_{f298}^\circ = - 11.1$	Barrow ⁸⁶

atoms. Thus if the heats of formation of all the species involved are known or estimated, the bond energies can be calculated. Employing the heats of formation of species $\text{AlCl}_3(\text{g})$, $\text{AlCl}_2(\text{g})$ and $\text{AlCl}(\text{g})$ given in the "JANAF" tables⁸⁸ the dissociation energies of the molecules have been calculated and are given in Table IIIa.

Table IIIa

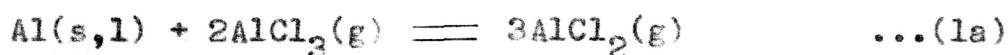
Dissociation profile of $\text{AlCl}_3(\text{g})$

Bond energy E(Kcal/mole)	Sequence	Dissociation energy H(Kcal/mole)
101.21	$\text{AlCl}_3 \rightarrow \text{AlCl}_2 + \text{Cl}$	93.21
105.21	$\text{AlCl}_2 \rightarrow \text{AlCl} + \text{Cl}$	92.81
117.61	$\text{AlCl} \rightarrow \text{Al} + \text{Cl}$	117.61

The heat of sublimation of Al and the dissociation energy of $\text{Cl}_2(\text{g})$ are taken from Brewer⁸⁹ and Gaydon⁵⁴ respectively. The bond energy term E is for undissociated species and is simply the atomic heat divided by the number of bonds. The above values indicate that the more stable species would be $\text{AlCl}(\text{g})$. However, the reliability of the heat of formation of $\text{AlCl}_2(\text{g})$ is doubtful and being an odd electron molecule AlCl_2 is likely to be unstable.

3.1.7. Free energy considerations

If one assumes AlCl(g) as the main and stable species the reaction between the aluminium chloride and aluminium metal will follow according to the equation (1). On the other hand if AlCl_2 is the main species in the reaction it may proceed according to the equation



If both aluminium monochloride and dichloride have the same stability the reaction will be:



It was therefore thought necessary to calculate the free energies for all the three reactions. Employing the data from 'JANAF' tables⁸⁸ these were calculated and are recorded in Table IIIb. The results of these calculations suggest that both AlCl(g) and $\text{AlCl}_2(\text{g})$ may exist as indicated by the large negative values of free energies for the reactions 1(a) and 1(b). However, there is no spectroscopic evidence for the existence of AlCl_2 species in appreciable concentration.

3.2. EXPERIMENTAL

Materials

Aluminium wire having 99.98% purity (BDH.AR quality) was melted in an argon atmosphere to expel the dissolved gases and the resulting ingot was cut into chips. These chips were degreased and used. Spectrographic analysis of

Table - IIIB

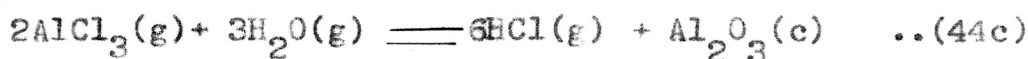
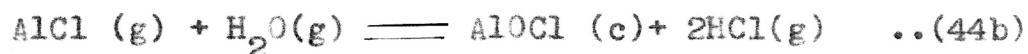
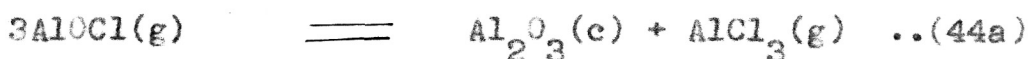
Free energies calculated from 'JANAF' tables for possible reactions

Temp. °K	$2\text{Al}(l) + \text{AlCl}_3(g) \rightleftharpoons 3\text{AlCl}(g)$	$\text{Al}(l) + 2\text{AlCl}_3(g) \rightleftharpoons 3\text{AlCl}_2(g)$	$\text{Al}(l) + \text{AlCl}_3(g) \rightleftharpoons \text{AlCl}_2(g) + \text{AlCl}(g)$	$3\text{AlCl}_2(g) + \text{Al}(l) \rightleftharpoons 3\text{AlCl}(g) + \text{AlCl}_3(g)$
1000	33.836	6.073	13.303	27.763
1100	27.577	1.829	9.802	25.748
1200	21.381	- 2.376	6.335	23.756
1300	15.236	- 6.533	2.901	21.769
1400	9.145	-10.675	- 0.504	19.802
1500	3.097	-14.739	- 2.239	17.840
1600	- 2.900	-18.796	- 7.232	15.896

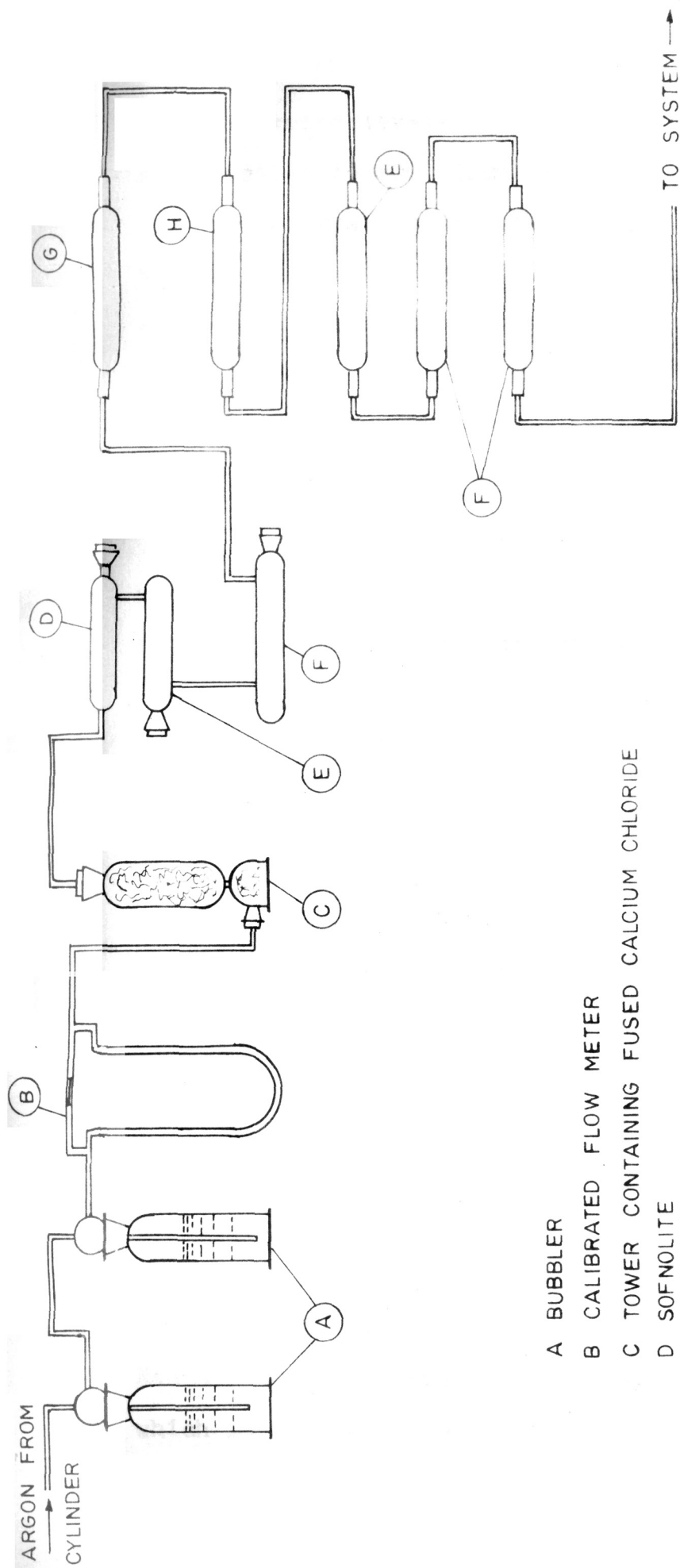
the sample indicated that it contained trace impurities (≈ 200 ppm) viz. Fe, Cu and Si. Aluminium chloride with 99.9% purity (E.Merck grade) was resublimed in an inert atmosphere before use. Resublimed product contained 0.04% ferric chloride and 0.02% alumina.

3.2.1. Purification of argon

Argon was used as a carrier gas. It was necessary to purify argon, as the impurities like oxygen, nitrogen and moisture would react with aluminium or with monochloride or trichloride as given below, thus affecting the apparent concentrations:



In order to remove impurities present in the carrier gas, argon from a cylinder was passed through a purification train which is schematically represented in Fig.1. The train consists of bubbler (1A and 1A) containing pyrogallol and sulphuric acid respectively, a calibrated capillary flow meter (1B) to regulate the gas, a calcium chloride tower (1D), two feet long columns containing sofnolite (1D), anhydrone (1E) and phosphorous pentoxide (1F) to remove carbon dioxide and



- A BUBBLER
- B CALIBRATED FLOW METER
- C TOWER CONTAINING FUSED CALCIUM CHLORIDE
- D SOFNOLITE
- E ANHYDRONE
- F P_2O_5
- G COPPER GAUGE AT 700°
- F CALCIUM AND ALUMINIUM METAL AT 800°

FIG. 1. PURIFICATION TRAIN FOR ARGON GAS

moisture respectively, a tube containing reduced copper gauze heated to 600° (16) (to remove oxygen), a tube containing the boats of calcium turnings and aluminium metal at 670° (11) (to remove nitrogen and oxygen) and finally a column containing anhydrous and two columns containing P_2O_5 to remove moisture.

3.3. APPARATUS AND PROCEDURE

The attainment of equilibrium in transpiration experiments will depend upon the construction of the apparatus. Keeping in view the points mentioned earlier (Chapter 2.4) the apparatus was constructed and employed in the present study.

The reaction tube made of Kyanite refractory (high alumina refractory tube, supplied by Central Glass and Ceramic Research Institute, Calcutta, India) of 60 cm. length and 2 cm. internal diameter was introduced in a Kanthal wound tube furnace. The furnace was 55 cm. in length and wound in three circuits. The outer two circuits had the same resistance covering the same length (10 cm. each) were useful to minimize heat losses. The third circuit (middle circuit) had a length of 20 cms. The furnace gave a constant temperature zone ($\pm 3^{\circ}$) of 20 cm. length at temperatures between 1000 and 1425°K . Temperatures were attained by connecting Kanthal heating elements to variable voltage transformers, which in turn were connected to a 230 V main source through voltage stabilizers to maintain constant power supply. The constant temperature zone was long enough to accommodate a

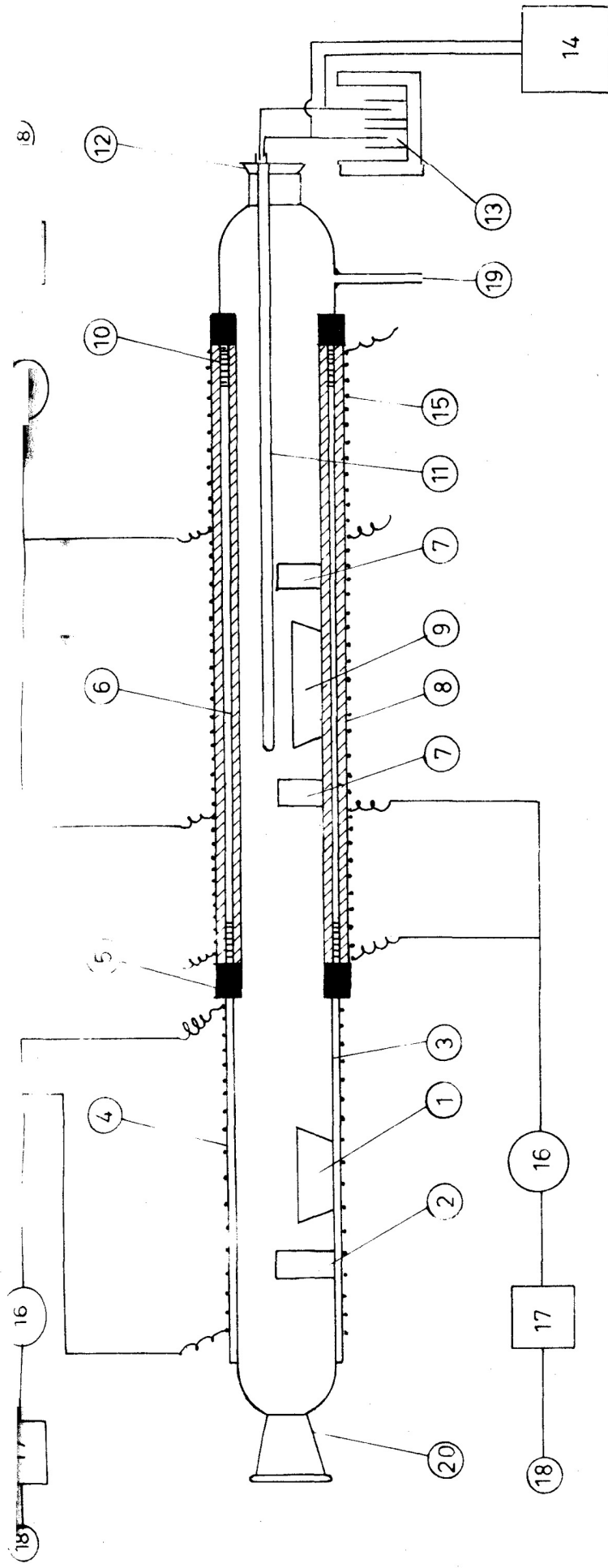
Kyanite boat of 15 cm. length, 1.5 cm. in width and 1.5 cm. height, leaving 6 to 8 cm. of zone for preheating the gases. This was useful in bringing all the reactants and the carrier gas to the equilibrium temperature. Two cylindrical alumina plugs were placed on either side of the boat. The annular 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 Kanthal heating elements consisted of light magnesia bricks. These bricks were of advantage in producing less massive and quicker heating furnace. These bricks can easily be worked out with a file. The furnace gave constant temperature over long periods of time ($\Delta T \approx 3^\circ$ 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 Associated Cement Company Ltd., India) to give cemented gas tight joints. In the pyrex tube at the upstream end (18" length and 1" i.d.) a glass boat (0.6" x 0.6" x 8") containing anhydrous aluminium chloride was introduced. Aluminium metal baffles on either side of the boat served as diffusion barriers. The temperature of the glass section was maintained at $150^\circ \pm 3^\circ$ to facilitate transport of the halide by argon gas. The stated uncertainty is the average temperature of all the runs reported, but the variation of temperature in each run is only $\pm 1^\circ$. Thus the

supply of aluminium trichloride was uniform and the deviation was not more than 5%. The AlCl_3 vaporization furnace was also connected to a variable voltage transformer through a voltage stabilizer. The furnace also had a sliding arrangement to facilitate arresting the reaction quickly by pushing it out after the run. From the down stream end a Kyanite thermocouple sheath entered the reaction tube and was positioned over the centre of the boat. A chromel-alumel thermocouple calibrated at various points (zinc, aluminium and copper, standard samples of these materials were procured from National Bureau of Standards, Washington, D.C., USA), served to measure the temperature during the reaction. Methods of calibration of thermocouples have been given by Rocser and Wensel⁹⁰. The temperatures were read by measuring the millivolts at intervals with a thermocouple test set, Cat. No: 7556, W.C. Pye and Co. Ltd., England. Initially, measurements were made of the actual boat temperature by insertion of thermocouple into the boat and compared with that by the thermocouple positioned above it. This difference was negligible as it was within the stated uncertainty. A schematic diagram of the transpiration apparatus has been given in Fig.2.

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 was found quite satisfactory.



- 1 AlCl_3 BOAT
- 2 ALUMINIUM METAL SHIELDS
- 3 PYREX GLASS ASSEMBLY (AlCl_3 VAPORIZATION CELL)
- 4 HEATING ELEMENTS (NICROME)
- 5 CEMENTED JOINTS
- 6 REACTION TUBE (KYANITE PASSIVATED OR ALUMINA)
- 7 ALUMINA SPACERS
- 8 FURNACE CORE (SILICA OR KYANITE)
- 9 SAMPLE BOAT
- 10 SUPPORTERS FOR REACTION TUBE

- 11 THERMOCOUPLE PROTECTION TUBE
- 12 RUBBER CORK
- 13 COLD JUNCTION
- 14 THERMOCOUPLE TEST SET
- 15 HEATING ELEMENTS (KANTHAL OR PLATINUM)
- 16 VARIABLE VOLTAGE TRANSFORMER
- 17 CONSTANT VOLTAGE STABILIZER
- 18 POWER SUPPLY
- 19 TO COLLECTOR
- 20 B₂₉ GLASS JOINT

FIG. 2. A SCHEMATIC DIAGRAM OF TRANSPARATION APPRATUS^A

In order to know the pressure in the system a by-pass from the outcoming gas flow was connected to a U-tube mercury manometer and the differences in heights were noted in a few experiments. These were 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 heights. The average of the total pressures in all the runs was around 720 mm.

The tube containing the sample boat was heated to the reaction temperature in a slow current of argon. The pyrex glass tube at the upstream end was also heated simultaneously to the desired temperature. When the temperatures reached the desired values and got stabilized the boat containing AlCl_3 was introduced. Precautions were taken to avoid diluting the carrier gas with air when inserting the boat in 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 the heating of aluminium trichloride was stopped. The system was allowed to cool in an argon atmosphere.

In each run the amount of AlCl_3 passed and the amount of chemically transported aluminium were found by weight loss measurements. A good agreement was noted between the loss in weight of the boat and the AlCl_3 collected. Loss in weight of aluminium was also checked by chemical analysis of the residual aluminium.

3.4. VAPORIZATION OF THE TRANSPORTING AGENT

The rate of transport of aluminium trichloride as a function of temperature and the rate of flow of argon gas were determined by a series of experiments. In each run good agreement was obtained between the loss in weight of the boat and AlCl_3 collected (analysed). The results are reported in Table IV. It can be seen from the table that the pressures show 10-20% deviation from those reported by Smits and Meijering⁹¹. This cannot be considered as serious in view of the complexity of the vaporization of aluminium trichloride⁹¹⁻⁹³. Smits and Meijering⁹¹ noted the difference in vapour pressure at the same temperature when different samples were used. Foster⁹² confirmed this and explained that this discrepancy was due to the slow rate of volatilization of aluminium trichloride at constant temperature. He also found that it is necessary to wait for a long time to attain the saturation pressure in the system, inspite of the high heat of vaporization of AlCl_3 . It can also be noticed from Table IV that as the flow rate is increased the deviation from the normal pressures also increased (slightly). This behaviour was also observed by Dunne and Gregory⁹³. In addition to these difficulties it is to be noted that the temperatures were measured only with a mercury thermometer which was not calibrated.

Table - IV

Comparison of the values of loss in weight
of AlCl_3 and AlCl_3 collected

Temp. °C	Flow rate cc./min.	AlCl_3 loss g.	AlCl_3 collected g.	Difference	% error
150	125	12.8470	12.6824	0.1646	1.28
150	76	9.6824	-	-	-
150	33	5.3368	5.2534	0.0834	1.56
168*	100	20.8362	-	-	-
168	85	19.2014	19.0956	0.1058	0.55
168	60	18.2486	18.0132	0.2354	1.29
134	30	1.8436	1.7804	0.0632	3.53
134	50	2.9812	2.7836	0.1976	7.09
134	100	3.5684	-	-	-
142	130	8.6290	-	-	-
142	60	5.7804	5.6426	0.1378	2.38
142	45	4.2232	4.1638	0.0594	1.43

* Run for only one hour

In view of the slow vaporization of aluminium trichloride, the long time needed to acquire saturation pressures in a large volume and the high flow rates involved, the above discrepancy need not be considered as serious. At pressures below 50 mm. of AlCl_3 the weight loss data and the collected amounts did not correspond well. This is attributed to the hydrolysis caused by very small amounts of moisture. Thus the ratio of the hydrolysed material and the transported chloride will be high particularly when the transport is low. As the pressures of AlCl_3 increase this becomes negligible. Hence runs were carried out only at partial pressures of normal halide above 50 mm.

Employing resublimed aluminium trichloride and careful handling of the sample it was observed that the hydrolysis was negligible indicating that the carrier gas was free of O_2 , H_2O , etc. The presence of these impurities in argon causes a white deposit of alumina in the tube.

3.5. ATTACK OF AlCl_3 ON THE CONTAINER MATERIAL

In a few preliminary experiments it was observed that the refractory boat (weight of the boat $\approx$ 16 grams) increased in weight at the end of a run of 2 hours. After each succeeding run, the increase in weight progressively reduced. The boat showed almost (less than 0.4%) negligible increase in weight after a total reaction period of 16-20 hours. Blank experiments carried out with aluminium metal or by transporting AlCl_3 vapour with an empty boat at 1183°K

showed no perceptible increase in the weight of the boat. In addition to the attack of aluminium monochloride on the boat material, it was observed that the inner surface of the Kyanite tube got covered with a thin layer of a black refractory material in the initial runs. To ensure complete passivation of the inner surface of the tube, a series of experiments were carried out by placing a number of boats containing aluminium metal throughout the length of the tube. Consistent results in the equilibrium studies could be obtained only after the two surfaces were passivated.

A small amount of black shining product as a result of this attack was collected. The behaviour of this material towards heat treatment and the reaction with aluminium monochloride vapour was studied. It did not show any loss in weight even after several hours of heating at about 1650°K , nor did it react with aluminium chloride vapour at 1300°K . Spectrographic analysis showed silicon, aluminium and iron as the major quantities (silicon excess) and Ni, Cu and Pb in traces (≈ 100 ppm each). Chemical analysis showed 81-83% silica, 14-15% alumina and 2-2.5% iron. Once the boat was covered with a film of the above black material, the equilibrium reaction between molten aluminium and aluminium chloride vapour could be studied over a wide temperature range (1125 - 1425°K) without any difficulty. The study of the reaction was carried out as follows:

- (1) Study of the reaction at constant partial pressure of AlCl_3 at one temperature as a function of the rate of flow of inert gas.
- (2) Study of the pressure dependence of the equilibrium constant for the assumed reaction at one temperature.
- (3) Study of the increase in the yield of the reaction by increasing its temperature at constant partial pressure of AlCl_3 .

3.6. TREATMENT OF THE DATA

In the study of equilibrium reaction (1) over the temperature range 1125-1425°K the experimentally determined weight loss data of Al and AlCl_3 were used to calculate the partial pressures AlCl and AlCl_3 . The vapour pressure of aluminium monochloride formed during the reaction at high temperatures was calculated from:

$$\frac{P_a}{P_t} = \frac{P_a}{P_a + P_b + P_f} = \frac{n_a}{n_a + n_b + n_f} \quad \dots(45)$$

where P_a = the partial pressure of AlCl , P_t = total pressure = 720 mm, n_a = number of moles of AlCl formed, n_b = number of moles of unreacted AlCl_3 , n_f is the number of moles of argon collected during the run.

The number of moles of AlCl formed (n_a), number of moles of unreacted AlCl_3 (n_b) and the number of moles of argon were obtained employing the following expressions respectively:

$$n_a = \frac{3/2 \times \Delta W \text{ Al}}{M \text{ Al}} \quad \dots(46)$$

$$n_b = \left(\frac{\Delta W \text{ AlCl}_3}{M \text{ AlCl}_3} \right) - \frac{1}{2} \frac{\Delta W \text{ Al}}{M \text{ Al}} \quad \dots(47)$$

$$n_f = \frac{V}{22.4} \quad \dots(48)$$

where $\Delta W \text{ Al}$ = aluminium metal transported g.

$\Delta W \text{ AlCl}_3$ = aluminium trichloride passed g.

M/Al = molecular weight of Al.

$M \text{ AlCl}_3$ = molecular weight of AlCl_3

V = volume of carrier gas collected in literes and at 298°K .

Similarly, partial pressure of $\text{AlCl}_3(\text{unreacted})$ was given by:

$$\frac{P_b}{P_t} = \frac{n_b}{n_a + n_b + n_f} \quad \dots(49)$$

The equilibrium constant for reaction 1 was calculated by substituting pressures into the expression:

$$K = \frac{P^3 \text{ AlCl}}{P \text{ AlCl}_3} \quad \dots(50)$$

3.7. EFFECT OF THE RATE OF FLOW OF ARGON ON THE EQUILIBRIUM BETWEEN $\text{AlCl}_3(\text{g})$ and $\text{Al}(\text{l})$

It is necessary to determine the limits of flow rates of the carrier gas which is saturated with the gaseous reaction products. This helps to know the extent to which the experimental results are being influenced by diffusion transport. If an equilibrium between a gas phase and a condensed phase is established with negligible diffusion

effects, the amount of vapour transported per unit time varies linearly with the flow rate of the gas mixture⁵⁹.

In the present experiment the transport of vapour is directly proportional to the loss in weight of the metal aluminium and hence it was studied at a reaction temperature of 1183°K by varying the flow rate of the carrier gas (containing AlCl_3 vapour) between 25 and $130\text{ cc}^3/\text{min}$. The vapour pressure of aluminium trichloride throughout these experiments was kept constant i.e. the temperature of the pyrex glass cell was maintained at 150° . When the weight loss data were plotted against the flow rate in the above range the weight loss increased linearly upto the rate of $107\text{ cc}^3/\text{min}$. thereby indicating that the flow gas was saturated with the gaseous reaction products and the equilibrium is independent of the flow of inert gas in this range. The curve on extrapolation passed through the origin showing that the thermal and self diffusion effects are negligible (Fig.3). The equilibrium constant calculated at each one of these flow rates between 25 and $107\text{ cc}^3/\text{min}$. agreed well ($\pm 2\%$) which also suggests that within these limits the reaction is independent of the flow rate of the carrier gas (Table V). Subsequently, all measurements were made below $107\text{ cc}^3/\text{min}$.

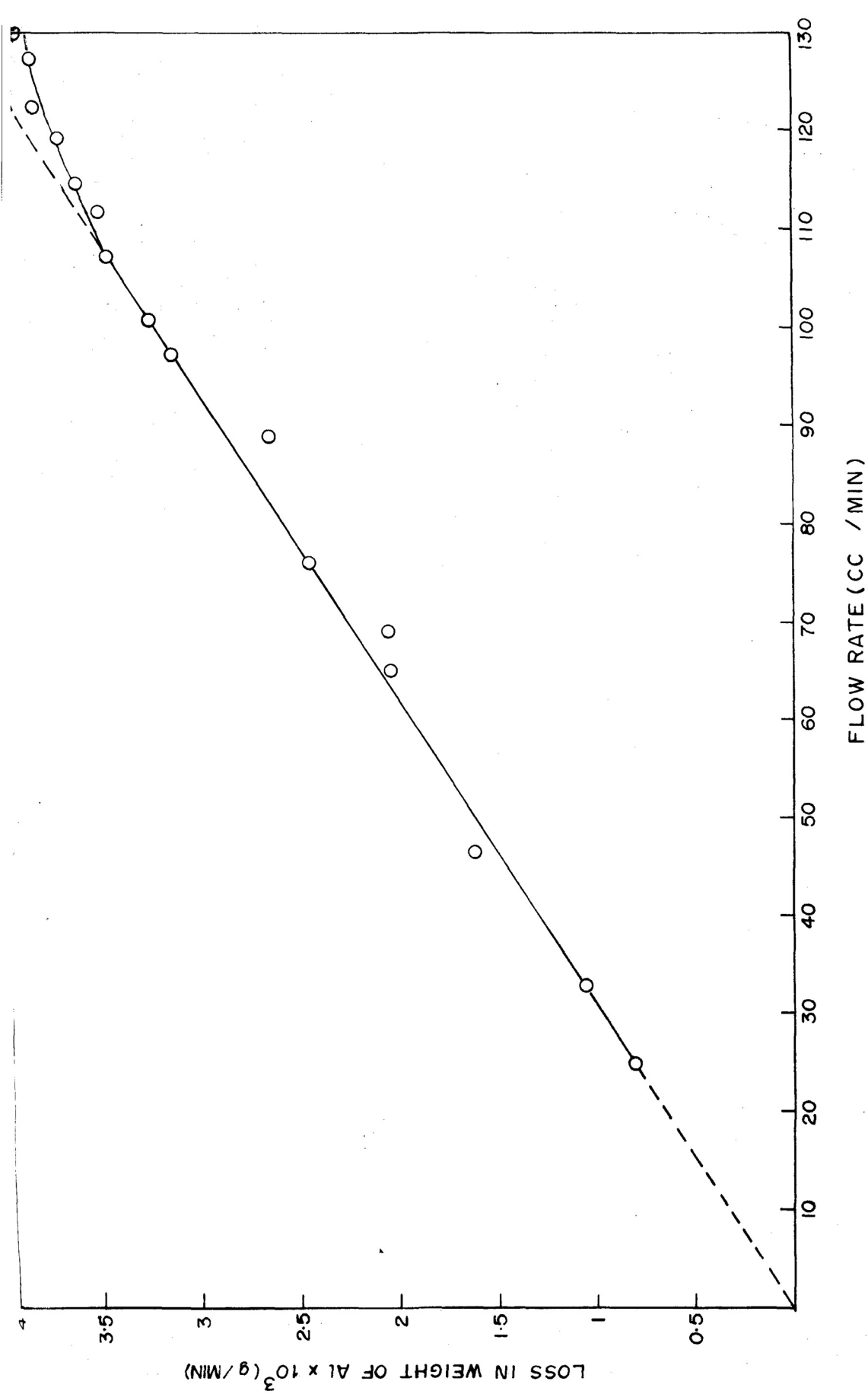


FIG.3- PLOT OF THE RATE OF AL. WT. LOSS VS. AlCl_3 FLOW RATE (ARGON GAS CONTG AlCl_3) FROM TRANPIRATION MEASUREMENTS AT 1183°K

Table - V

Transport of aluminium with change of flow rate and
calculated equilibrium constants

Flow rate c.c./min.	Time(min.)	Al trans- ported g.	AlCl ₃ passed g.	P AlCl(atm)	P AlCl ₃ (atm)	K _p	Log K _p
25	60	0.0502	2.0892	3.1284 x 10 ⁻²	1.6527 x 10 ⁻¹	1.8526 x 10 ⁻⁴	- 3.7321
33	120	0.1205	5.3368	3.1029 x 10 ⁻²	1.6071 x 10 ⁻¹	1.8589 x 10 ⁻⁴	- 3.7308
46.3	60	0.0960	2.9015	3.3875 x 10 ⁻²	1.2687 x 10 ⁻¹	3.0639 x 10 ⁻⁴	- 3.5137
60.5	120	0.2496	7.8475	3.3482 x 10 ⁻²	1.3079 x 10 ⁻¹	2.8697 x 10 ⁻⁴	- 3.5421
69.3	90	0.1845	7.0190	3.5098 x 10 ⁻²	1.3543 x 10 ⁻¹	3.1926 x 10 ⁻⁴	- 3.4958
76	100	0.2460	8.2142	3.1609 x 10 ⁻²	1.3180 x 10 ⁻¹	2.3962 x 10 ⁻⁴	- 3.6205
89	120	0.3172	10.6805	2.9389 x 10 ⁻²	1.3051 x 10 ⁻¹	1.9449 x 10 ⁻⁴	- 3.7111
97	120	0.3826	10.4740	3.2906 x 10 ⁻²	1.1055 x 10 ⁻¹	2.8469 x 10 ⁻⁴	- 3.5456
100	120	0.3929	11.7477	3.2401 x 10 ⁻²	1.2992 x 10 ⁻¹	2.1801 x 10 ⁻⁴	- 3.6622
107	60	0.2108	6.6815	3.2227 x 10 ⁻²	1.2704 x 10 ⁻¹	2.6346 x 10 ⁻⁴	- 3.5799

3.8. TRANSPORT OF ALUMINIUM AS A FUNCTION OF THE PARTIAL PRESSURE OF AlCl_3

A study of the pressure dependence of the equilibrium constant for the reaction (1) was carried out at 1183°K in order to find out the importance of other species during the reaction. The pressure of AlCl_3 was varied more than 5 times yet the change in equilibrium constant was found negligible. The results are indicated in Table VI. This was further confirmed by plotting $\log P \text{ AlCl}$ against $\log P \text{ AlCl}_3$ (Fig.4). A straight line with slope of 0.31 ± 0.04 was obtained when this was done. For AlCl_2 formation the values of the slopes as per equations 1a and 1b should be 0.67 and 1 respectively. Thus it is clear that $\text{AlCl}_2(\text{g})$ is not an important species in these experiments.

3.9. RESULTS AND DISCUSSION

Having established an equilibrium flow rate and showing the absence of the formation $\text{AlCl}_2(\text{g})$, the experimental determination of the transport of the aluminium metal as a function of temperature was carried out over the region of $1125\text{-}1425^\circ\text{K}$ keeping the aluminium trichloride partial pressure constant.

Eleven points were studied in this region. The experimental results together with the calculated vapour pressures of AlCl_3 , AlCl and equilibrium constants calculated according to the equation 50 are presented in Table VII. At each reaction temperature the AlCl_3 generation cell temperature

Table - VI

Study of the reaction $2\text{Al}(l) + \text{AlCl}_3(g) \rightleftharpoons 3\text{AlCl}(g)$ by changing the vapour pressure of AlCl_3

Time(min.)	AlCl_3 g.	Al trans- ported g.	Volume of argon pas- sed	$P_{\text{AlCl}}(\text{atm})$	$P_{\text{AlCl}_3}(\text{atm})$	K_p	Log K_p
120	2.6214	0.1284	5	liters	2.3143×10^{-2}	5.6097×10^{-2}	2.2131×10^{-4} - 3.6550
120	3.1032	0.2015	9.6	"	2.3101×10^{-2}	4.0303×10^{-2}	3.0588×10^{-4} - 3.5145
120	5.7804	0.2156	7.2	"	3.0472×10^{-2}	1.00×10^{-1}	2.8295×10^{-4} - 3.5484
60	2.0892	0.0502	1.5	"	3.1284×10^{-2}	1.6527×10^{-1}	1.8526×10^{-4} - 3.7321
120	11.7477	0.3929	12	"	3.2418×10^{-2}	1.5684×10^{-1}	2.1801×10^{-4} - 3.6322
120	10.6805	0.3172	10.68	"	2.9389×10^{-2}	1.3051×10^{-1}	1.9449×10^{-4} - 3.7111
120	10.8900	0.2497	7.32	"	3.1900×10^{-2}	1.7561×10^{-1}	1.8483×10^{-4} - 3.7350
60	21.0245	0.3835	6.00	"	4.5941×10^{-2}	3.2414×10^{-1}	2.9914×10^{-4} - 3.5242

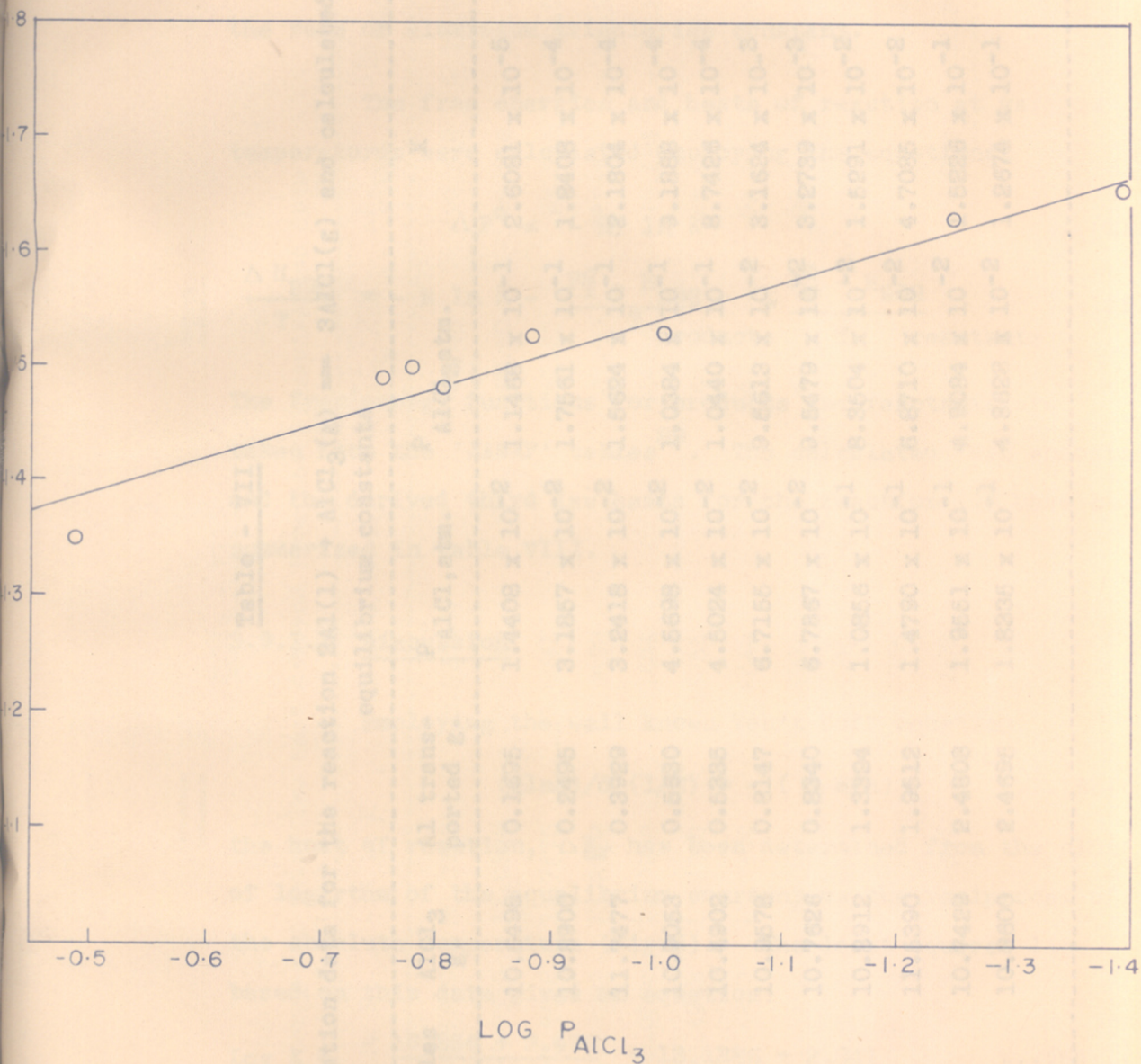


FIG. 4 - PLOT OF LOG P_{AlCl_3} Vs LOG. P_{AlCl_3}

Table - VII

Transpiration data for the reaction $2\text{Al}(l) + \text{AlCl}_3(g) \rightleftharpoons 3\text{AlCl}(g)$ and calculated equilibrium constants

Temp. K	No. of moles of argon	AlCl_3 g.	Al trans-ported g.	$P_{\text{AlCl, atm.}}$	$P_{\text{AlCl}_3, \text{ atm.}}$	K	Log K
1125	0.5358	10.6495	0.1695	1.4408×10^{-2}	1.1468×10^{-1}	2.6081×10^{-5}	- 4.5839
1183	0.3247	10.8900	0.2435	3.1857×10^{-2}	1.7561×10^{-1}	1.8408×10^{-4}	- 3.7350
1183	0.5358	11.7477	0.3929	3.2418×10^{-2}	1.5624×10^{-1}	2.1804×10^{-4}	- 3.6622
1220	0.5464	10.9053	0.5630	4.5698×10^{-2}	1.0384×10^{-1}	9.1888×10^{-4}	- 3.0368
1225	0.5258	10.4902	0.5335	4.5024×10^{-2}	1.0440×10^{-1}	8.7426×10^{-4}	- 3.0584
1270	0.5464	10.9578	0.8147	6.7155×10^{-2}	9.5613×10^{-2}	3.1624×10^{-3}	- 2.4993
1280	0.5358	10.7626	0.8340	6.7867×10^{-2}	9.5479×10^{-2}	3.2739×10^{-3}	- 2.4850
1336	0.5454	10.8912	1.3324	1.0856×10^{-1}	8.3504×10^{-2}	1.5291×10^{-2}	- 1.8157
1373	0.5358	11.5390	1.9512	1.4790×10^{-1}	6.8710×10^{-2}	4.7085×10^{-2}	- 1.3271
1420	0.4958	10.7429	2.4808	1.9551×10^{-1}	4.9084×10^{-2}	1.5226×10^{-1}	- 0.8174
1425	0.5358	10.9600	2.4695	1.8335×10^{-1}	4.8628×10^{-2}	1.2674×10^{-1}	- 0.8972

was measured and a blank run was carried in order to keep the rate of aluminium trichloride constant.

The free energies and heats of reaction at various temperatures were calculated employing the equations:

$$\Delta F^{\circ} = - RT \ln K \quad \dots(51)$$

$$\frac{\Delta H_{298}}{T} = - R \ln K - \frac{F_T^{\circ} - H_{298}}{T}_{\text{products}} + \frac{F_T^{\circ} - H_{298}}{T}_{\text{reactants}} \quad \dots(52)$$

The free energy functions for products and reactants are taken from the 'JANAF' tables⁸⁸. The calculated free energies and the derived third law heats for the reaction (1) have been summarized in Table VIII.

3.9.1. Discussion

Employing the well known Van't Hoff equation

$$(d \ln K) / d (1/T) = - (\Delta H / R) \quad \dots(53)$$

the heat of reaction, ΔH_r has been determined from the plot of logirthm of the equalibrium constant vs the reciprocal of the absolute temperature (Fig.5). The least squares line based on this data gives an equation:

$$\text{Log } K = - \frac{19.856 + 3.496}{T} + 13.1386 \pm 2.841 \quad \dots(54)$$

The constants from equation (54) lead to a value of ΔH_r heat of reaction $\Delta H_r = 90.86 \pm 1.6 \text{ Kcal.mole}^{-1}$. This value of ΔH_r represents the mean value over the temperature range

Table - VIII

Free energy and third law heat derived from the transpiration data

Temp. °K	Log K	- R ln K	- RT ln K Kcal.	$-\Delta \frac{F_T - H_{298}}{T}$	ΔH_{f298}	ΔH_{f298}
1125	-4.5839	20.9750	23.5969	67.48	99.512	- 12.015
1183	-3.7350	17.0906	20.2182	67.20	99.716	- 11.947
1183	-3.6622	16.7575	19.8241	67.20	99.322	- 12.078
1220	-3.0368	13.8958	16.9529	67.00	98.693	- 12.288
1225	-3.0584	13.9946	17.1434	66.98	99.194	- 12.121
1270	-2.4993	11.4363	14.5251	66.76	99.309	- 12.082
1280	-2.4850	11.3709	14.5548	66.72	99.356	- 11.867
1336	-1.8157	8.3083	11.0999	66.74	99.864	- 11.897
1373	-1.3271	6.0725	8.3375	66.24	99.285	- 12.090
1420	-0.8179	3.7384	5.3085	66.02	99.057	- 12.166
1425	-0.8972	4.1054	5.5802	66.02	99.900	- 11.885
					Avr. - 12.040 ±	0.10
					Standard error of mean = 0.10	
					Standard deviation = 0.210	

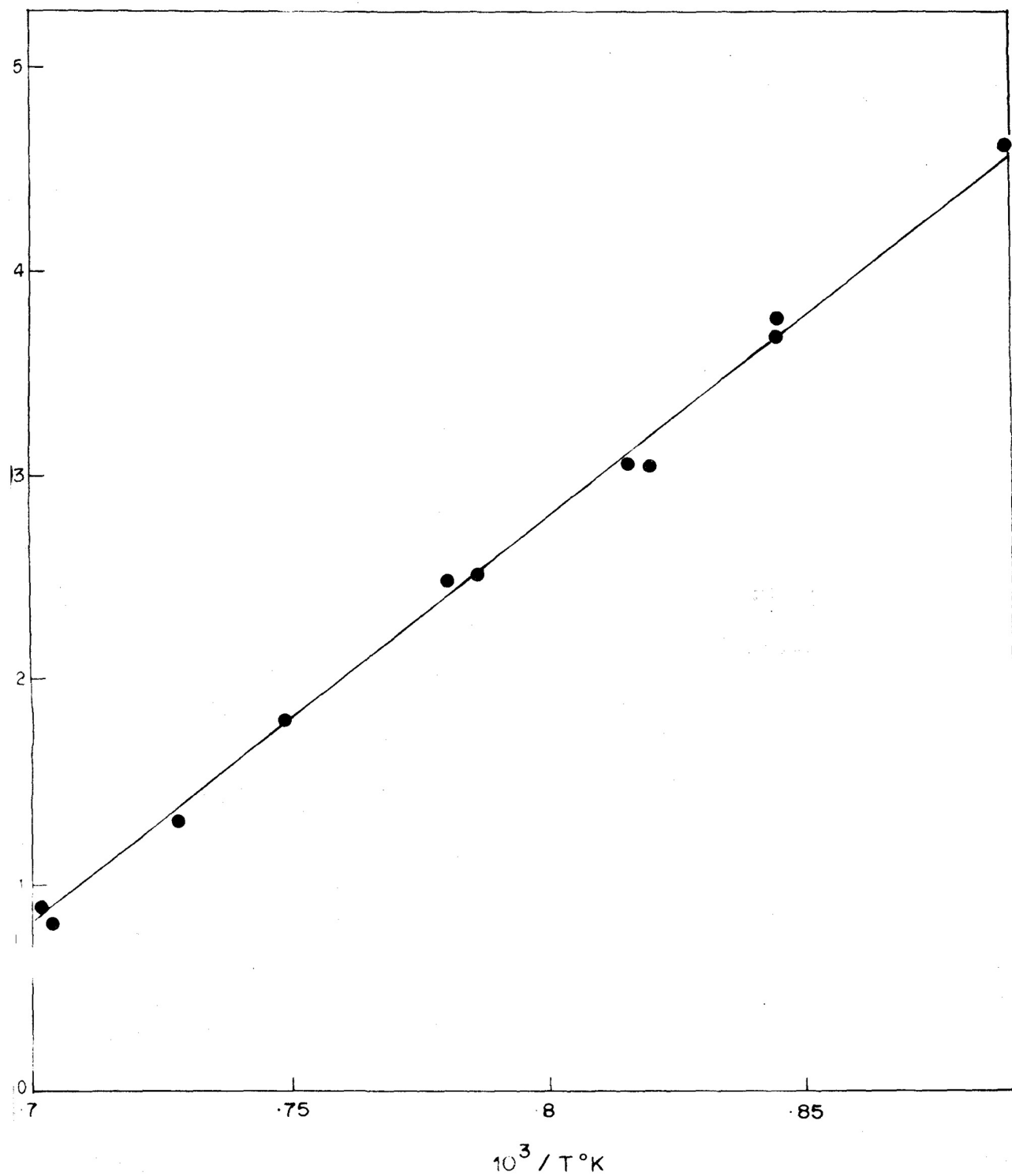


FIG. 5- PLOT OF LOG K VS. $1/T$ FROM TRANSFERATION STUDIES OF
THE REACTION $2 \text{Al}_{(l)} + \text{AlCl}_{3(g)} \rightleftharpoons 3 \text{AlCl}_{(g)}$

studied and does not take into account the effect of Δc_p . From the functions cited in the 'JANAF' tables⁸⁸ $\Delta(H_{1275} - H_{298})$ for reaction (1) has been found to be - 7.34 Kcal. The $\Delta H_{-T_{298}}$ thus becomes 98.20 ± 1.6 Kcal.mole⁻¹ which is in satisfactory agreement with the corresponding third law value 99.44 Kcal.mole⁻¹. The slight deviation from the third law heat may be due to the temperature dependent errors which contribute significantly to the third law calculations. The second law heat of reaction thus permits the heat of formation of AlCl(g) to be calculated from the equation:

$$\Delta H_{f_{298}} \text{AlCl(g)} = \frac{1}{3} \Delta H_{r_{298}} + \Delta H_{f_{298}} \text{AlCl}_3(\text{g}) + \Delta H_{f_{298}} 2\text{Al} \dots (55)$$

as -12.45 ± 0.54 Kcal.mole⁻¹ and the corresponding third law value gives -12.04 ± 0.22 Kcal mole⁻¹. The uncertainties reported in this work are only those due to the statistical analysis of the data. The $\Delta H_{f_{298}}$ values for AlCl₃(g) and Al(l) have been taken from the 'JANAF' Tables⁸⁸. To facilitate comparison, log K values at different temperatures reported by several workers have been recorded in Table IX.

3.10. THE ENTROPY OF THE REACTION

The entropy ΔS_r of the reaction is obtained from the second law of thermodynamics

$$\Delta F_r = \Delta H_r - T \Delta S_r \dots (56)$$

Employing the values of ΔF_r and ΔH_r at 1275°K, a value of 60.12 ± 1.3 cal.deg.⁻¹ mole⁻¹ for ΔS_r 1275 is obtained.

Table - IX

Comparison of the values for equilibrium constants
(log K)

		Temp. °K				Ref.
1000	1100	Log	K	1300	1500	
- 7.1	- 5.3			- 2.5	- 0.4	81
- 5.3	- 4.8			- 1.4	+ 0.3	82
- 6.94	- 5.09			- 2.25	- 0.17	46
- 5.5	- 3.8			- 1.1	- 0.9	84
- 7.1	- 5.2			- 2.4	- 0.4	85
- 7.71	- 5.91			- 3.15	- 1.13	94
- 6.76	- 4.96			- 2.18	- 0.14	Present work

This value agrees well with the theoretical value of $\Delta S_{r1273} = 60.5 \text{ cal.deg.}^{-1} \text{ mole}^{-1}$ reported by Heimgartner⁸⁰ and also agrees well with $\Delta S_{r1275} = 61.26 \text{ cal.deg.mole}^{-1}$, calculated from the data given in the 'JANAF' tables⁸⁸.

While this work was under study, Frisch et.al.⁹⁴ have also studied and reported the reaction (1) over the temperature range 930-1034°K employing a different method known as the molecular flow effusion technique. An excellent agreement has been noted between their data and that of the present work. These authors have also derived the entropy of $\text{AlCl}_3(\text{g})$ from the entropy of reaction (1) and the value of ΔS_{982} for $\text{AlCl}_3(\text{g})$ is essentially 4 cal./deg./mole higher than the estimated value⁸⁸. They have concluded that the value of ΔS_{298}^0 for $\text{AlCl}_3(\text{g})$ is given in the 'JANAF' tables⁸⁸ is uncertain by at least 2 cal./deg./mole. They have given some experimental evidence based on the study of the work of several authors on the vapour pressures of AlCl_3 . In some cases (Smits and Meijering⁹¹) experimental entropy differs only by one cal./deg./mole from that of the calculated value⁸⁸.

The $\Delta S_{r1275} = 60.12 \pm 1.3 \text{ cal./deg./mole}^{-1}$ reported in the present work agreed well with the calculated value and the difference is within the stated uncertainties. The excellent agreement between second and third law heats and a good agreement between the experimental and calculated entropies suggest that the entropy of $\text{AlCl}_3(\text{g})$ at elevated temperatures

may have considerable validity. The results of the present work are in good agreement with those reported by Gross et.al.⁴⁶ as can be seen from Table IX. It also shows that the presence of AlCl_2 species (as suggested by Heimgartner⁸⁰) is not important in the temperature range studied. In view of the observations of Frisch et.al.⁹⁴ on the entropy of aluminium trichloride, it is to be mentioned that a revision of the functions of $\text{AlCl}_3(\text{g})$ may be of great help.

$$\Delta H_f^\circ \text{ at } 298^\circ \text{K} = -14.20 \pm 1.5 \text{ kcal/mole}^\circ$$

$$\Delta H_f^\circ \text{ at } 298^\circ \text{K Third law} = -32.44 \pm 0.54 \text{ kcal/mole}^\circ$$

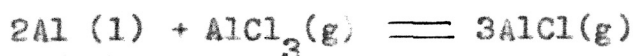
$$\Delta H_f^\circ \text{ at } 298^\circ \text{K Second law} = -33.20 \pm 1.5 \text{ kcal/mole}^\circ$$

$$\Delta H_f^\circ \text{ at } 298^\circ \text{K for AlCl(g) (Third law)} = -12.04 \pm 0.57 \text{ kcal/mole}^\circ$$

$$\Delta H_f^\circ \text{ at } 298^\circ \text{K for AlCl(g) (second law, w)} = -11.41 \pm 0.54 \text{ kcal/mole}^\circ$$

Table - X

Thermodynamic data for the reaction



$$\Delta H_r \text{ at } 1275 = 90.86 \pm 1.6 \text{ Kcal. mole}^{-1}$$

$$\Delta S_r \text{ at } 1275 = 60.12 \pm 1.3 \text{ cal./deg./mole}$$

$$\Delta F_r \text{ at } 1275 = 14.20 \pm 1.5 \text{ Kcal. mole}^{-1}$$

$$\Delta H_r \text{ at } 298 \text{ Third law} = 99.44 \pm 0.66 \text{ Kcal.mole}^{-1}$$

$$\Delta H_r \text{ at } 298 \text{ Second law} = 98.20 \pm 1.6 \text{ Kcal.mole}^{-1}$$

$$\Delta H_f \text{ at } 298 \text{ for AlCl(g) (third law)} = -12.04 \pm 0.22 \text{ Kcal.mole}^{-1}$$

$$\Delta H_f \text{ at } 298 \text{ for AlCl(g) (second law)} = -12.45 \pm 0.54 \text{ Kcal.mole}^{-1}$$

CHAPTER - 4

Section - A

REACTION OF $\text{AlCl}_3(\text{g})$ WITH $\text{MgO}(\text{c})$ AND THE
HEAT OF FORMATION OF $\text{MgAl}_2\text{O}_4(\text{c})$

1. INTRODUCTION

Though the vapour phase existence of aluminium monochloride has been already established, very little is known about its reaction with MgO . The reaction of AlCl_3 with MgO has been studied by several workers.

CHAPTER - 4

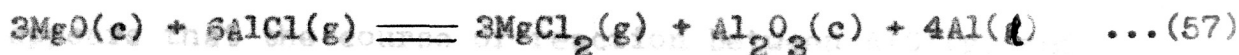
Section - A

REACTION OF $\text{AlCl}_3(\text{g})$ WITH $\text{MgO}(\text{c})$ AND THE
HEAT OF FORMATION OF $\text{MgAl}_2\text{O}_4(\text{c})$.

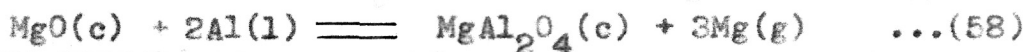
CHAPTER - 4

Section - AREACTION OF $\text{AlCl}(\text{g})$ WITH $\text{MgO}(\text{c})$ AND THEHEAT OF FORMATION OF $\text{MgAl}_2\text{O}_4(\text{c})$ 4.1. INTRODUCTION

Though the vapour phase existence of aluminium monochloride and its highly reducing nature has been realized long back⁷³, very little is known about its action on refractory oxides, Semenovitch⁹⁵ has reported that aluminium monochloride reacted with refractory oxides viz. MgO , BeO , ZrO_2 and SiO_2 but not with Al_2O_3 . His experiments were purely qualitative. He has also suggested the following mechanism for the reaction of aluminium monohalide with $\text{MgO}(\text{c})$ at 1100°C .

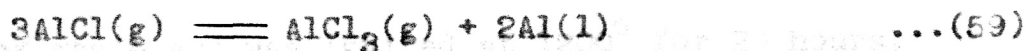


The possibility of aluminium metal reacting with $\text{MgO}(\text{c})$ was not taken into consideration. Altman^{96,97}, and Grjotheim, Herstad and Toguri⁹⁸ have measured the vapour pressures of magnesium metal in the temperature range of $1143\text{--}1414^\circ\text{K}$ by studying the reaction:



This suggests the formation of the spinel $\text{MgAl}_2\text{O}_4(\text{c})$, in the reaction of $\text{AlCl}(\text{g})$ with $\text{MgO}(\text{c})$ at these temperatures which was overlooked by Semenovitch⁹⁵. The presence of

aluminium metal also reduces the magnesium chloride with the formation of aluminium chloride at these temperatures as was indicated in the work of Balduin⁹⁹. Reduction of magnesium chloride is also possible by $\text{AlCl}(\text{g})$ as the unstable molecules will always provide aluminium metal due to the reversibility of reactions (1)



Preliminary experiments showed that the reaction yielded more MgAl_2O_4 (product) with increase of temperature. This suggests that the equilibrium reaction is endothermic and must occur with an increase of entropy according to the principle of successive entropy states⁴⁴. In this connection, Brewer⁴³ had also stated that a gas will only react endothermically with a solid to produce a significant yield of reaction product if the reaction produces at least as many moles of gas as are consumed, in the reaction. Thus it appears that the course of reaction between $\text{AlCl}(\text{g})$ and $\text{MgO}(\text{c})$ is not according to that indicated by Semenkovich⁹⁵ and hence the necessity for the present investigation.

In continuation of the study of the equilibrium reaction (Chapter 3)



the gaseous monochloride was allowed to react with solid MgO . In order to establish the reaction scheme, equilibrium

measurements were carried out together with the identification of the products.

4.2. EXPERIMENTAL SECTION

(A) Materials

The magnesium oxide used in this investigation was of E.Merck grade and was ignited at 1200° for 20 hours. The powder was pressed into briquettes at 1000 kg/cm^2 . The briquettes were broken into small pieces (sieve size of 80 US) to give rise to a sample with large surface area which ensures equilibrium with the carrier gas. Aluminium chloride was also of E.Merck grade and was resublimed in an inert atmosphere before use. The material was always handled in a dry box. Aluminium metal used in the production of monochloride was of spectrographically standard grade and was supplied by Johnson Mathey and Co. Ltd., London.

(B) Apparatus and general procedure

The apparatus and the method adopted to study the reaction between the gaseous monochloride and magnesium oxide was similar to that described in Chapter 3. The general principles involved in the chemical transportation have also been discussed in Chapter 2. In this method the carrier gas argon saturated with aluminium monochloride was allowed to react with MgO(c) under equilibrium conditions. The products

were identified by x-ray and spectrographic methods. The amount of MgO taking part in the reaction was determined by the analysis of the residue in the boat. The gaseous products of the reaction carried away by the argon gas were also analysed. The boats used in these reactions were of passivated Kyanite as was described in Chapter 3. The reaction tube (at temperatures above 1425°K was of alumina for temperatures less than 1425°K , passivated Kyanite tube was employed) which was surrounded by a platinum wire-wound tube furnace. The furnace wound in three circuits gave a constant zone of about 10 to 11 inches within $\pm 7^{\circ}$ and gave temperatures upto 1550°K . The zone was sufficient to accommodate two 5 inch long boats containing aluminium metal and magnesium oxide respectively. Radiation shields were placed on both sides of the boats. This was found necessary as AlCl_3 brought in with argon may react with MgO before it equilibrates with Al . The temperatures were measured with a calibrated chromel-alumel thermocouple. At temperatures above 1200°K , a Pt-Pt 10% Rh thermocouple was used. After the experimental run of one or two hours, the heating of aluminium chloride was stopped and the system cooled in the argon gas flow. The boats were finally pushed to a chamber containing dry nitrogen and weighed. The residue in the second boat was powdered in a dry box and analysed for $\text{MgAl}_2\text{O}_4(\text{c})$.

4.3. IDENTIFICATION OF THE PRODUCTS

The residue in the boat was examined for its solid phase by studying its x-ray powder pattern. A sample of the residue was sealed in a glass capillary tube of 0.5 to 0.6 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., Regaku Denki Co. Ltd., 8 Kanda-Dai dokaro-cho Chigada-ku, Tokyo, Japan) mounted in an x-ray unit. The unit had a copper target (The Machlett Laboratories Inc., USA) with nickel foil filter was used to obtain the x-ray beam at 50 kv.v. and 18 mA. Powder pattern showed the formation of spinel MgAl_2O_4 (g). Search for MgO (c) and Al_2O_3 revealed that excess MgO (unreacted) was present and the lines did not disclose 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 pattern of the residue with that given in the ASTM index¹⁰⁰. The incorporation of excess Al_2O_3 in the spinel lattice reduces the lattice parameters^{101, 102} while a similar incorporation of MgO increases¹⁰³ lattice parameters. In this case the MgO is in large excess therefore slight increase in the d values were noted. The x-ray data are

4.5. Reaction of Residue with H_2O

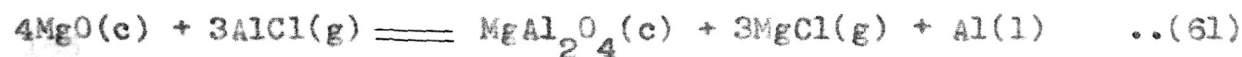
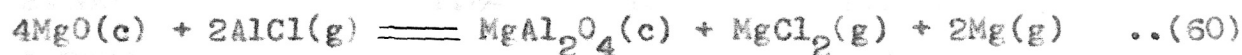
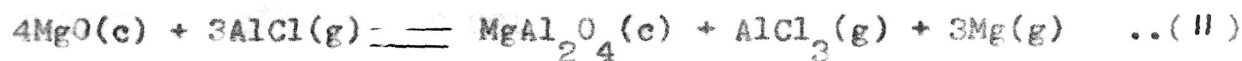
The reaction (Al) can be referred to the reaction

two facts viz. that the reaction of Al_2O_3 with H_2O is

given in Table XI. The principal d values which are associated with MgO and MgAl_2O_4 are given here. Apart from the lines reported here some faint lines were observed which are most probably due to impurities. Lines corresponding to alumina phase were not present confirming its absence.

4.4. POSSIBLE EQUILIBRIUM REACTIONS

Considering the presence of magnesium aluminate as one of the products of the reaction the experimental data were examined to determine the possibility of one of the following reactions:



The above reactions are possible according to the thermodynamic generalizations^{43,44} mentioned previously. In these cases $\text{AlCl}(\text{g})$ reacts endothermically with $\text{MgO}(\text{c})$ and the entropy is positive with increase of temperature. The free energies of the above reactions as a function of temperature are tabulated in Table XII and have been calculated from the 'JANAF' tables⁸⁸.

4.5. THE EQUILIBRIUM REACTION

The reaction (61) can be rejected on the basis of two facts viz: that the $\text{MgCl}(\text{g})$ is not important at these temperatures and also that the highly reducing nature of the

Table - XI

Prominent x-ray diffraction lines of the products of reaction(11)

Time of exposure - 15 hours

Radiation: Cu K α , Nickel

foil filter

Experimental		ASTM index for MgAl ₂ O ₄		ASTM index for MgO	
dA°	Relative intensity	dA°	Relative intensity	dA°	Relative intensity
		4.67	4	2.431	10
2.9284	M	2.858	40	2.106	100
2.4479	SM	2.436	100	1.489	52
2.3611	M	2.333	3	1.270	4
2.1160	S ⁺⁺	2.021	58	1.216	12
2.030	M	1.649	10	1.0533	5
1.7977	W	1.555	45	0.9665	2
1.6631	M	1.429	58		
1.5007	S ⁺	1.366	3		
1.4387	M	1.278	2		
1.4088	VW	1.232	9		
1.2775	M	1.218			
1.2200	SM	1.166	7		
1.1741	W	1.131	2		
1.0594	M	1.0796	4		
0.9713	M				

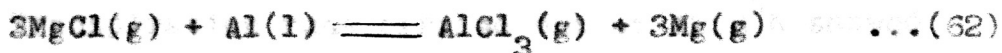
Table - XII

Free energies calculated from the 'JANAF' tables⁸⁸

Temp. °K	Free energies Kcal			
	Reaction(11)	Reaction(60)	Reaction(61)	Reaction(62)
1000	12.137	1.080	22.149	- 10.012
1100	11.006	- 0.766	21.546	- 10.540
1200	9.842	- 2.631	20.909	- 11.067
1300	8.683	- 4.525	20.283	- 11.600
1400	7.527	- 6.309	19.645	- 12.118
1500	6.336	- 8.160	18.994	- 12.658

The boat containing MgO and $MgAl_2O_4$ was carefully weighed. The difference in weight was noted and the substance in the boat was completely transferred to a mortar and the empty boat was weighed. The material was well ground and an aliquot was fused ^{with} pyrophosphate. The fused mass was extracted with dilute acid and analyzed for aluminum and magnesium by usual methods. Thus the amount of MgO reacted was calculated.

aluminium metal causes the reaction



The free energies of the reaction (62) (table XII) also indicate that the reaction (61) can be neglected under conditions of these experiments. Identification of the products and equilibrium measurements are helpful in the examination of reactions (11) and (60).

The products collected were resublimed in a dry nitrogen atmosphere at 200°C. The sublimate was found to be AlCl_3 . The absence of chloride in the residue showed that MgCl_2 was not the product of reaction, consequently reaction (11) may be the only possible equilibrium reaction.

4.6. ANALYSIS

The boat containing MgO and MgAl_2O_4 was carefully weighed. The difference in weight was noted and the substance in the boat was completely transferred to a mortar and the empty boat was weighed. The material was well ground and an aliquot was fused ^{with} pyrosulphate. The fused mass was extracted with dilute acid and analysed for aluminium and magnesium by usual methods. Thus the amount of MgO reacted was calculated.

4.7. TREATMENT OF THE DATA

Transpiration runs carried out at 1336°K showed that the flow rates of argon upto 180 ml./min. were satisfactory. The results are recorded in Table XIII. The previous study of the equilibrium reaction (1) (Chapter 3) showed that the effects of self and thermal diffusions were negligible at these flow rates.

The vapour pressures of $\text{AlCl}(\text{g})$, $\text{AlCl}_3(\text{g})$ and $\text{Mg}(\text{g})$ were calculated from the experimentally determined weight losses of $\text{Al}(\text{l})$ and $\text{MgO}(\text{c})$. Assuming that the ideal gas law holds good, in the equilibrium zone, the partial pressures of the various components are calculated as follows:

$$\begin{aligned} P_{\text{AlCl}} &= \text{Pressure AlCl generated} \\ &= \frac{3/2 \ n_{\text{Al}} \ RTr}{V_r} \quad \dots(63) \end{aligned}$$

$$P_{\text{AlCl}_3} = \frac{1/4 \ n_{\text{MgO}} \ RTr}{V_r} \quad \dots(64)$$

$$P_{\text{Mg}} = \frac{3/4 \ n_{\text{MgO}} \ RTr}{V_r} \quad \dots(65)$$

$$P_{\text{AlCl}}^{\text{unreacted}} = (n_{\text{AlCl}} - 3/4 \ n_{\text{MgO}}) \frac{RT_r}{V_r} \quad \dots(66)$$

The pressure of the unreacted AlCl_3 in the reaction (which produces AlCl) was taken into account while calculating equilibrium constant of the reaction (2). This was necessary because AlCl_3 was one of the products of

Table XIII

Effect of flow rate on the reaction $4\text{MgO}(c) + 3\text{AlCl}(g) \rightleftharpoons \text{MgAl}_2\text{O}_4(c) + \text{AlCl}_3(g) + 3\text{Mg}(g)$
at 1336°K

Time (min.)	Flow rate (cc/min)	ΔW AlCl_3	ΔW Al g.	ΔW MgO g.	P_{AlCl_3} atm.	P_{Mg} atm.	P_{AlCl} atm.	K
120	150	5.85	1.49	2.42	4.24×10^{-2}	6.12×10^{-2}	5.16×10^{-2}	7.27×10^{-2}
80	180	3.45	1.28	2.28	2.73×10^{-2}	7.12×10^{-2}	4.97×10^{-2}	8.03×10^{-2}
120	120	4.02	1.19	2.09	3.57×10^{-2}	6.59×10^{-2}	4.84×10^{-2}	8.98×10^{-2}

the reaction between $\text{AlCl}(\text{g})$ and $\text{MgO}(\text{c})$. The pressure of unreacted AlCl_3 in the reaction (1) was given by

$$P_{\text{AlCl}_3}^* = (n_{\text{AlCl}_3} - 1/2 n_{\text{Al}}) \frac{RT}{V_r} \quad \dots(67)$$

The total pressure of AlCl_3 in the reaction was:

$$P'_{\text{AlCl}_3} = P_{\text{AlCl}_3} + P_{\text{AlCl}_3}^* \quad \dots(68)$$

The equilibrium constant

$$K_p = \frac{(P_{\text{Mg}}^3)(P_{\text{AlCl}_3})}{P_{\text{AlCl}}^3} \quad \dots(69)$$

The experimental results and calculated equilibrium constants are given in Table XIV. The reaction between $\text{AlCl}_3(\text{g})$ and $\text{MgO}(\text{c})$ was negligible in comparison to $\text{AlCl}(\text{g})$. It may be stated here that the dimer $\text{Al}_2\text{Cl}_6(\text{g})$ is not an important species at these temperatures of study.

4.8. RESULTS AND DISCUSSION

The free energy and third law heats were calculated employing the following relations:

$$\begin{aligned} \Delta F_T &= -RT \ln K_p \\ \Delta H_{298} &= T \left[-\Delta \frac{F_T^0 - H_{298}^0}{T} - R \ln K_p \right] \quad \dots(70) \end{aligned}$$

The free energy functions for $\text{AlCl}(\text{g})$, $\text{AlCl}_3(\text{g})$ and $\text{Mg}(\text{g})$ were taken from the 'JANAF' tables⁸⁸. Thermal functions for $\text{MgAl}_2\text{O}_4(\text{c})$ were taken from Bonnickson¹⁰⁴. The third

Table - XIV

Experimental data for the reaction $4\text{MgO}(c) + 3\text{AlCl}(g) \rightleftharpoons 3\text{MgAl}_2\text{O}_4(c) + \text{AlCl}_3(g) + 3\text{Mg}(g)$

T°, K	$t, \text{min.}$	$\Delta W \text{ Al, g.}$	$\Delta W \text{ MgO, g.}$	$P_{\text{AlCl}_3}, \text{atm.}$	$P'_{\text{AlCl}_3}, \text{atm.}$	$P_{\text{Mg}}, \text{atm.}$	$P_{\text{AlCl}}, \text{atm.}$	$K_p, \text{atm.}$
1298	100	0.8187	1.4460	1.4053×10^{-2}	1.9069×10^{-2}	4.2159×10^{-2}	2.9184×10^{-2}	5.7487×10^{-2}
1321	100	1.1535	2.0100	1.9530×10^{-2}	2.3402×10^{-2}	5.8590×10^{-2}	4.1913×10^{-2}	6.3925×10^{-2}
1336	80	1.2813	2.2550	2.3742×10^{-2}	2.7342×10^{-2}	7.1226×10^{-2}	4.9728×10^{-2}	8.0342×10^{-2}
1372	90	1.6092	2.8060	3.2233×10^{-2}	3.6166×10^{-2}	9.6714×10^{-2}	6.9058×10^{-2}	9.9338×10^{-2}
1398	120	2.3092	3.8660	4.6526×10^{-2}	4.9922×10^{-2}	1.3958×10^{-1}	1.0957×10^{-1}	1.0320×10^{-1}
1428	80	1.9850	3.2650	6.1877×10^{-2}	6.5178×10^{-2}	1.8563×10^{-1}	1.5150×10^{-1}	1.1990×10^{-1}
1465	60	2.1180	3.6540	7.8916×10^{-2}	8.4558×10^{-2}	2.3675×10^{-1}	1.7335×10^{-1}	2.1541×10^{-1}

law calculations for reaction (11) are given in Table XV and they yielded an average heat of $\Delta H_{298} = 21.85 \pm 0.84$ Kcal. mole⁻¹.

To overcome the wide scattering of the points in the second law plot of $\log K$ vs $1/T$ a $\sum$ plot treatment^{67,68} was employed (Fig.6). The heat capacities for Mg(g), AlCl(g), MgO(c), AlCl₃(g) and MgAl₂O₄(c) are taken from Stull and Sinke¹⁰⁵, Kelley¹⁰⁶, Dingmann¹⁰⁷ and Bonnickson¹⁰⁴, respectively. The $\sum$ plot of this data gives an equation:

$$\log K_p = - \frac{4615.5 \pm 545}{T} + 2.18 \log T - 0.87 \times 10^{-4} T - 0.54 \times 10^5 T^{-2} - 4.3636 \pm 0.39 \dots (71)$$

The heat of reaction from $\sum$ plot is given by:

$$\Delta H_T^0 \text{ (Kcal.mole}^{-1}\text{)} = 21.12 + 4.33 \times 10^{-3} T - 0.40 \times 10^{-6} T^2 + 4.94 \times 10^2 T^{-1} \dots (72)$$

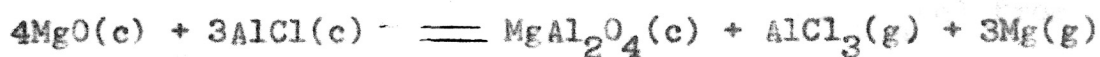
The constants from equation 72 lead to a value of

$\Delta H_{298} = 24.03 \pm 2.49$ Kcal.mole⁻¹. The second law value is in satisfactory agreement with that of the third law (21.85 ± 0.84 Kcal. mole⁻¹). The difference of 2.18 Kcal. may be due to the errors dependent on temperatures. The variation of $\pm 7^\circ$ will cause a discrepancy of 2.65 Kcal. in the second law and 0.1 Kcal. in the third law.

Combining the heat of reaction with the heats of formation of AlCl₃(g), MgO(c), AlCl(g) and Mg(g) from the 'JANAF' tables⁸⁸, one obtains a value of $\Delta H_{298} = -553.36 \pm 1.89$ Kcal. mole⁻¹ for the third law value and $-551.18 \pm$

Table - XV

Thermodynamic properties of the reaction



$T^\circ\text{K}$	$\text{Log } K_p$	$\Delta F, \text{Kcal/mole}^{-1}$	$-\Delta \frac{F_T^\circ - H_{298}^\circ}{T}$	$\Delta H_{298} \text{ Kcal mole}^{-1}$
1298	- 1.2404	7.37	11.28	22.01
1321	- 1.1943	7.22	11.28	22.12
1336	- 1.0951	6.69	11.28	21.78
1372	- 1.0029	6.30	11.29	21.79
1398	- 0.9864	6.31	11.29	22.09
1428	- 0.9212	6.02	11.29	22.14
1465	- 0.6668	4.47	11.29	21.01

Avr. = 21.85 + 0.84
Kcal.

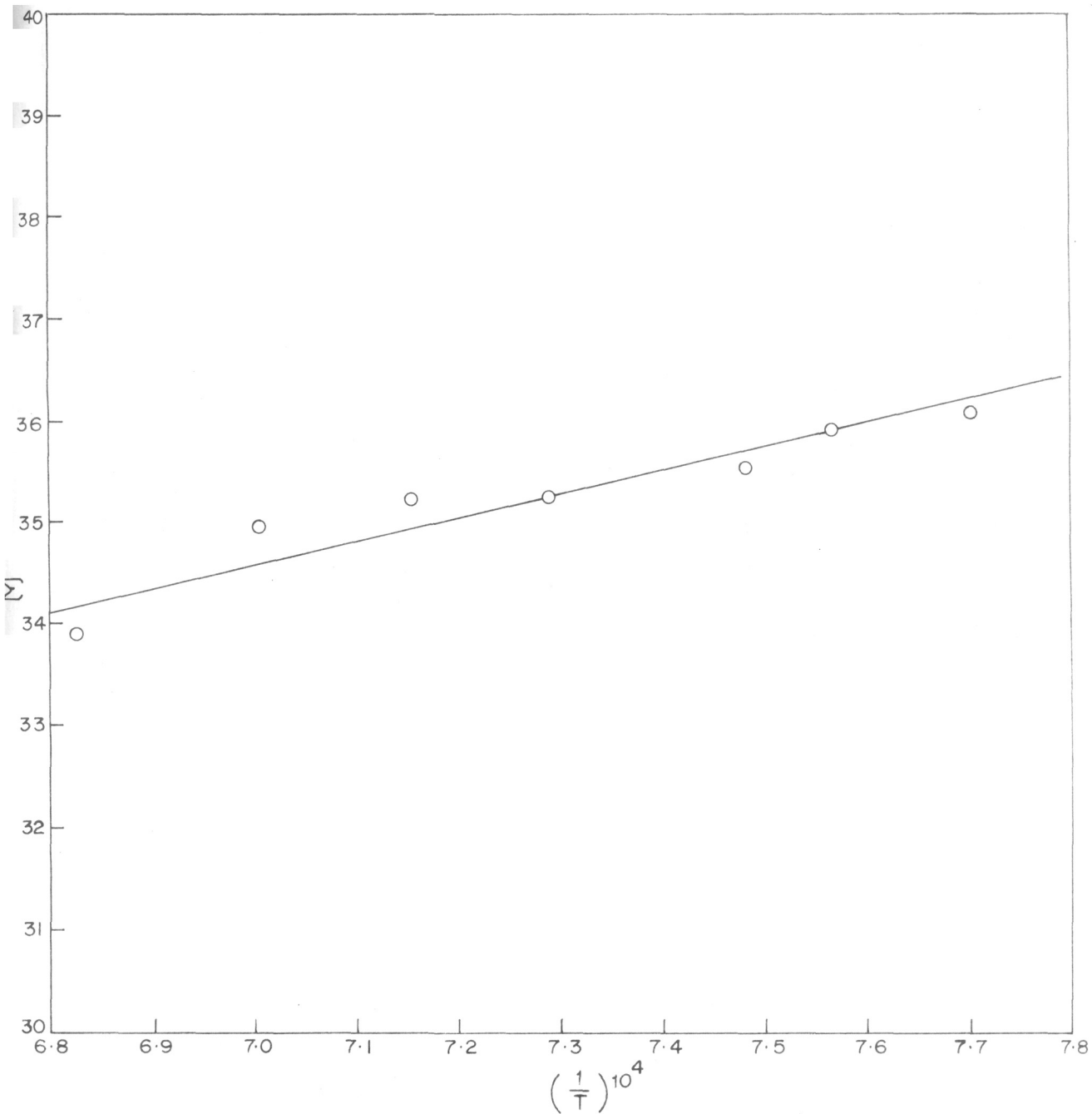


FIG. 6 - Σ PLOT FOR THE REACTION, $4 \text{MgO}_{(c)} + 3 \text{AlCl}_{(g)} \rightleftharpoons \text{MgAl}_2\text{O}_{4(c)} + \text{AlCl}_{3(g)} + 3 \text{Mg}_{(g)}$

3.55 Kcal. mole⁻¹ for the second law value; for the heat of formation of magnesium aluminate, from its elements. These give $\Delta H_{298} = -9.26 \pm 1.89$ and -7.08 ± 3.55 Kcal. mole⁻¹ respectively for the formation of $\text{MgAl}_2\text{O}_4(\text{c})$ from the oxides:



The values are in excellent agreement with the values obtained by Altman⁹⁶, Grjotheim, Herstad and Toguri⁹⁸, and Novrotsky and Kleppa¹⁰⁸. The pressures of magnesium are slightly less than those reported by Grjotheim⁹⁸ et.al.

4.9. ENTROPY OF THE REACTION

A plot of ΔF vs T (Fig.7) yields a value for the entropy of reaction. Least squares data lead to a value of $\Delta S_{1393} = 14.96 \pm 2.6$ cal.deg.⁻¹ mole⁻¹. This compares favourably with the theoretical value of 11.8 cal.deg.⁻¹ mole⁻¹ calculated from the 'JANAF' tables⁸⁸. The difference may be due to the experimental difficulties or due to the uncertainty of entropy of AlCl_3 as reported by Frisch et.al.⁹⁴. However, previous study (Chapter 3) showed that the entropy of AlCl_3 may have considerable validity at higher temperatures. It is felt that revision of the entropy of $\text{AlCl}_3(\text{g})$ will lead to a clearer understanding of these problems.

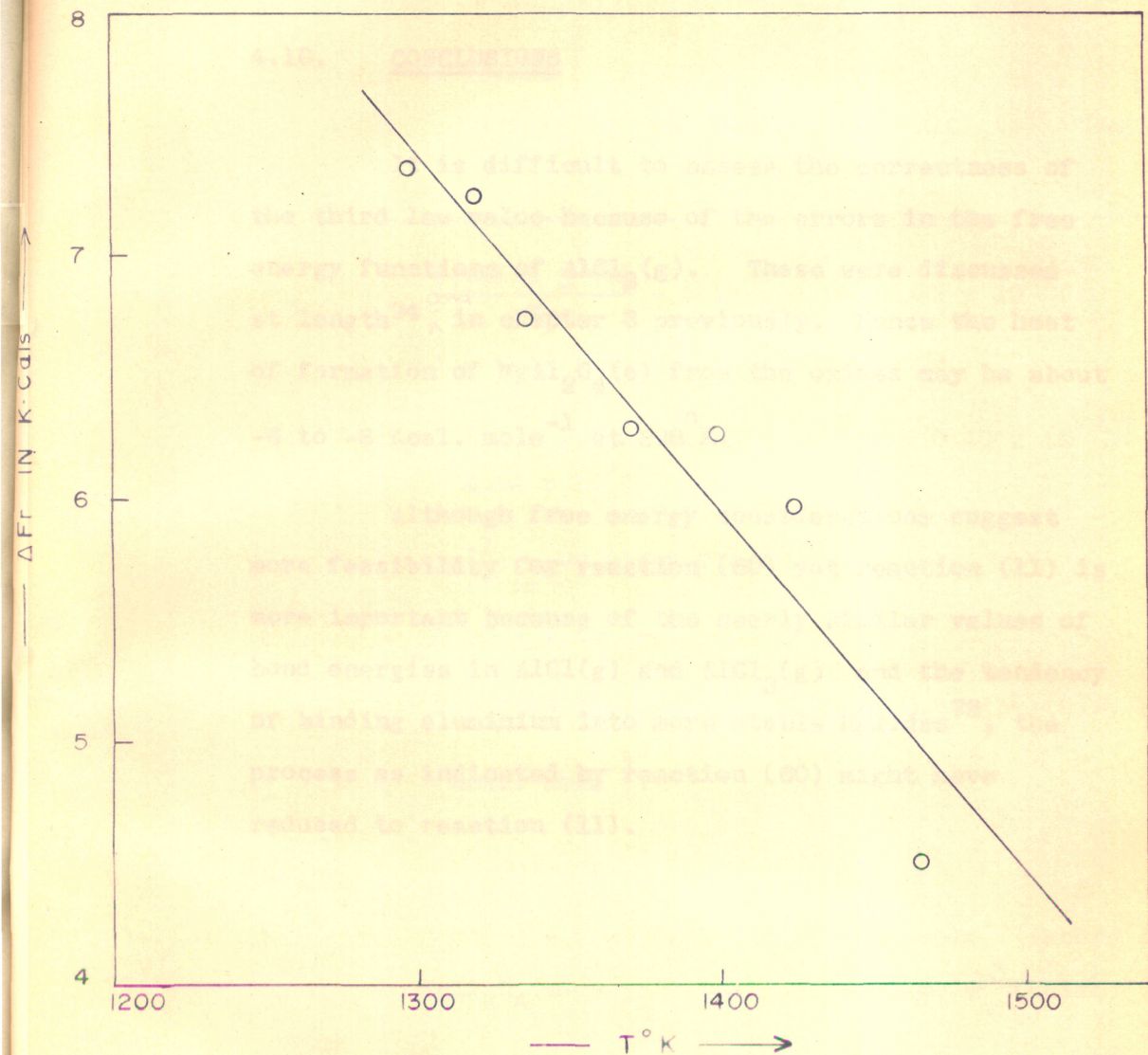


FIG. 7- THE ΔF_r FOR THE REACTION $4MgO_{(c)} + 3AlCl_{3(g)} = MgAl_2O_{4(c)} + AlCl_{3(g)} + 3Mg_{(g)}$
AS A FUNCTION OF TEMPERATURE

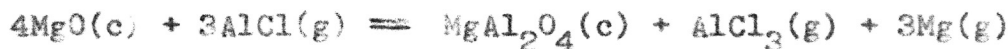
4.10. CONCLUSIONS

It is difficult to assess the correctness of the third law value because of the errors in the free energy functions of $\text{AlCl}_3(\text{g})$. These were discussed at length⁹⁴ ^{and} in chapter 3 previously. Hence the heat of formation of $\text{MgAl}_2\text{O}_4(\text{c})$ from the oxides may be about -6 to -8 Kcal. mole⁻¹ at 298° K.

Although free energy considerations suggest more feasibility for reaction (60) yet reaction (11) is more important because of the nearly similar values of bond energies in $\text{AlCl}(\text{g})$ and $\text{AlCl}_3(\text{g})$ and the tendency of binding aluminium into more stable halides⁷⁸, the process as indicated by reaction (60) might have reduced to reaction (11).

Table - XVI

THERMODYNAMIC DATA FOR THE REACTION



$$\text{Log } K_p = - \frac{4,615.5 \pm 545}{T} + 2.18 \log T - 0.87 \times 10^{-4} T - 0.54 \times 10^5 T^{-2} - 4.3636 \pm 0.39$$

$$\Delta H_T^\circ (\text{Kcal.mole}^{-1}) = 21.12 + 4.33 \times 10^{-3} T - 0.40 \times 10^{-6} T^2 + 4.94 \times 10^2 T^{-1}$$

$$\Delta F_T (\text{Kcal.mole}^{-1}) = -0.01496 T \pm 26.90.$$

$$\Delta H_{1382} = 26.70 \pm 2.49 \text{ Kcal. mole}^{-1}.$$

$$\Delta H_{298} = 24.03 \pm 2.49 \text{ Kcal.mole}^{-1}, 21.85 \pm 0.84 \text{ (by third law).}$$

$$\Delta F_{1382} = 6.22 \text{ Kcal. mole}^{-1}.$$

$$\Delta S_{r1382} = 14.96 \text{ cal.deg.}^{-1} \text{ mole}^{-1}.$$

$$\Delta H_{f298} \text{ for MgAl}_2\text{O}_4(\text{c}) = -551.18 \pm 3.55 \text{ Kcal.mole}^{-1} \text{ (second law).}$$

$$\text{MgAl}_2\text{O}_4(\text{c}) = -553.36 \pm 1.89 \text{ Kcal.mole}^{-1} \text{ (third law).}$$

$$\Delta H_{f298} \text{ for MgAl}_2\text{O}_4 \text{ from oxides} = -7.08 \pm 3.55 \text{ Kcal.mole}^{-1} \text{ (2nd law)}$$

$$\text{MgAl}_2\text{O}_4 \text{ from oxides} = -9.26 \pm 1.89 \text{ Kcal.mole}^{-1} \text{ (3rd law)}$$

the study of the reaction of $AlCl_3(g)$ with $MgAl_2O_4(c)$

CHAPTER - 4

Section - B

REACTION OF $AlCl_3(g)$ with $MgAl_2O_4(c)$

CHAPTER - 4

Section - BREACTION OF $\text{AlCl}(\text{g})$ WITH $\text{MgAl}_2\text{O}_4(\text{c})$ 4 B 1. INTRODUCTION

The formation of spinel MgAl_2O_4 was observed during the study of the reaction of $\text{AlCl}(\text{g})$ with $\text{MgO}(\text{c})$ (Chapter 4). The spinels have been found to be very useful refractories as lining materials in the steel manufacture because of their properties to withstand the attack of slags. The magnesia spinel has a limited application as a commercial refractory material because of the expense of making a high purity product which will compete with other refractories.

The methods available in the literature for the preparation of magnesium aluminate are:

- (A) Heating stoichiometric amounts of pure hydrated alumina and magnesia for several hours including a total of 15 hours at $1450-1500^\circ\text{C}$.¹⁰⁹ The pelleted mixture of oxides should be heated, followed by intervening grindings, mixings, chemical analyses and adjustments of composition. Though the compound with 99.5% purity can be obtained by this method, it is time consuming. The use is limited when the spinel is made by sintering the mixture of both oxides¹¹⁰, as they undergo a considerable increase in volume and the mixture was not suitable for refractory purposes.

spinel formation occurring at the inter-face pushes the gains apart. However, this property of the spinel has been put to good use when it is used as a liner in the induction furnaces.

(B) Magnesium aluminate can also be obtained by aluminothermic reduction of magnesium oxide in the temperature range of 1150-1450°K⁹⁷. Altman⁹⁶ observed that the weight loss is significant when a mixture of Al-MgO is heated at 1300°K whereas the loss in weight of the sample of Al-MgAl₂O₄ mixture is negligible at these temperatures. If the reaction between AlCl and MgAl₂O₄ is negligible at these temperatures pure magnesium aluminate can be prepared by heating the mixture of Al-MgO(Al in excess) at 1300°K and driving out the excess aluminium via AlCl(g). In the transport reactions the reactants need not be taken in stoichiometric ratios and the composition of the product is determined by analysis. The excess constituent can also be transported chemically after the reaction is complete. This chapter gives some experimental results of the reaction of AlCl(g) and AlCl₃(g) with a synthetic sample of magnesium aluminate.

4 B 2. EXPERIMENTAL

(A) Materials

The magnesia spinel was prepared in the manner described by King¹⁰⁹. Alumina (BDH AnalaR) and magnesia (E. Merck grade) were mixed in a stoichiometric ratio and the mixture was ball milled and pressed into pellets. This

mixture was heated for 60 hours at $1350-1400^{\circ}$ and finally for 3 hours in a hot pot furnace at $1500-1600^{\circ}$. The x-ray powder pattern of the sample agreed with that given for MgAl_2O_4 in the ASTM catalogue¹⁰⁰. Analysis of the sample gave 27.48% magnesia and 72.45% alumina (calculated values are 28.34% and 71.66% respectively). A slight excess of alumina does not affect the present study as it does not react with $\text{AlCl}_3(\text{g})$.

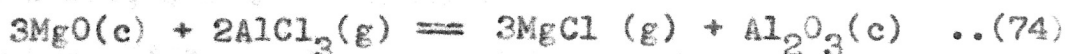
In the study of the reaction of AlCl_3 with a mixture of Al and MgAl_2O_4 , aluminium metal used was grease free coarse powder supplied by BDH Ltd. The purity of the sample was 99.99.5%. It was also necessary to carry out the runs with aluminium metal which had not been purified by heating to drive off volatile impurities. The metal powder was degreased by treatment with thiophene-free benzene in a soxhlet extractor for 8-10 hours. Traces of moisture were removed by heating the metal at 400° under vacuum. The sample when melted separately in an inert atmosphere, showed nearly 1.0% of insoluble matter which was mainly oxide.

(B) Apparatus and procedure

The apparatus and general procedure were the same as used in the experimental work described in Chapter 3 and chapter 4, section A. The flow rates of 100 to 180 ml./min. were used and found satisfactory.

(C) Results

When aluminium trichloride (≈ 6 gms. per hour) at a diluent gas flow rate of 130 cc/min. was passed over synthetically prepared sample of MgAl_2O_4 (≈ 4 gms.) for 2 hours at 950° no appreciable amount of reaction was observed. Further the sample on analysis also showed the original composition. However, under similar experimental conditions $\text{AlCl}_3(\text{g})$ was found to react with $\text{MgO}(\text{c})$. The extent of reaction was nearly four times less than the theoretically calculated for the reaction



The cause for this low reactivity may be due to the non-equilibrium condition or the kinetic effects.

When aluminium trichloride was allowed to react first with aluminium metal kept in a separate boat prior to the boat containing magnesium aluminate the monochloride formed reacted negligibly with MgAl_2O_4 at temperatures around 950° . But a slight increase in the weight of the boat was noted and was found to be due to the aluminium metal which might have come out of disproportionation of aluminium monochloride. This kind of observation is not uncommon in the study of the unstable halides by transpiration experiments. Small temperature gradients which are unavoidable in a temperature zone of 20-25 cm. may cause AlCl to disproportionate to some extent. After the

experiment the sample was washed with warm dilute hydrochloric acid (1.25 N) and the residue analysed. Below 900°C hardly 2% reaction was observed. The extent of reaction increased to about 12% at 1140° . The x-ray powder pattern of the resulting sample showed the presence of Al_2O_3 . The results are given in Table XVII.

A few experiments were carried out by mixing known amounts of aluminium metal with magnesium aluminate and passing AlCl_3 over the mixture. Results are given in Table XVIII, and they indicate substantial quantities of aluminium metal can be removed by passing $\text{AlCl}_3(\text{g})$ over a mixture of spinel and aluminium metal at temperatures around 900° . The removal of the metal is due to the formation of $\text{AlCl}(\text{g})$. However, the product on analysis showed slight excess of alumina content of the spinel and may be due to impurity present in the aluminium metal. It is possible to separate the spinel from the aluminium metal successfully by carrying out this reaction at temperatures around 900° (above 900° $\text{AlCl}(\text{g})$ reacts with $\text{MgAl}_2\text{O}_4(\text{c})$).

It can also be concluded that the reaction between AlCl and MgAl_2O_4 was much less than that between AlCl and MgO at the temperature range of study.

Table - XVIIReaction of AlCl_3 with MgAl_2O_4 (c)

Temp. °C	Flow rate ml./min.	$\Delta W \text{AlCl}_3$ g.	$\Delta W \text{Al}$ g.	ΔW of the sample	% of Al_2O_3
850 hrs.	150 Al taken	15 MgAl_2O_4 taken	0.45	+ 8	73.56
975	130	8	0.58	- 2	74.85
1020 2	11 1.6897	12 1.7015	0.72 0.772	+ 6	75.10
1080 2	100 1.0260	6 1.8071	0.96 0.7494	- 14	77.24
1180 3	100 0.3124	8 1.6105	1.58 0.6700	- 25	79.26

In each run the magnesium aluminate sample taken was about 3 gms.

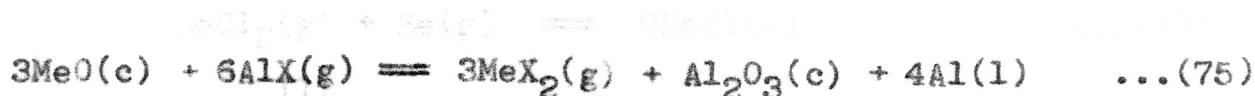
Table - XVIIIReaction of AlCl (g) with a mixture of $\text{Al-MgAl}_2\text{O}_4$

Temp. °C	Time hrs.	Wt.of Al taken	Wt.of MgAl_2O_4 taken	ΔW of the sample	% of Al_2O_3
1010	2	1.8897	2.7015	0.9873	75.54
900	2	1.0260	1.8075	0.5459	73.96
850	3	0.3124	1.5105	0.2700	73.04

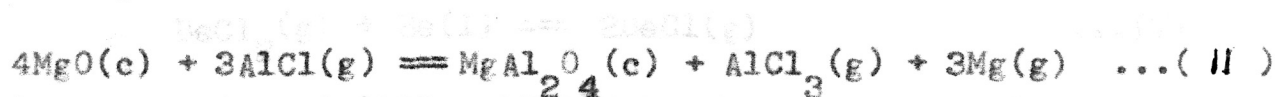
CHAPTER - 5

REACTION OF $\text{AlCl}(\text{g})$ WITH $\text{BeO}(\text{c})$ AND THE
HEAT OF FORMATION OF BERYLLIUM MONOCHLORIDE5.1. INTRODUCTION

Semenkovitch⁹⁵ studied the reaction of aluminium subhalide vapours with many refractory oxides but the equilibrium reactions presented are doubtful. The following mechanism was suggested by him for the reaction of the subhalide with magnesium and beryllium oxides



However, the previous study of reaction of $\text{AlCl}(\text{g})$ with $\text{MgO}(\text{c})$ (Chapter 4) revealed that the reaction proceeds through the scheme



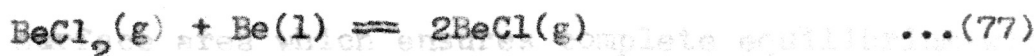
where the formation of magnesia spinel was observed. According to the free energy given by Semenovitch⁹⁵ (-170 Kcal.) $\text{AlCl}(\text{g})$ reacts extensively with $\text{BeO}(\text{c})$. But the strong resisting nature of the oxide towards reduction (its reaction even with carbon and liquid aluminium is negligible at 1400°K) shows that the extent of the reaction proposed by Semenovitch⁹⁵ might be doubtful. Considering the possibility of beryllium aluminate, the reaction of monochloride with solid beryllium oxide was attempted.

Preliminary experiments on this reaction at 1398° K showed not only the formation of beryllium aluminate, but also gave evidence for the formation of beryllium monochloride as major species. The study therefore provides useful data for the determination of the heat of formation of BeCl(g) as well as establishing the reaction scheme.

The only experimental values available for the heat of formation of beryllium monochloride was given by the work of Hildenbrand, Theard and Ju¹¹¹ and Greenbaum et.al.¹¹² in which they studied the equilibrium of the reaction



These results¹¹¹ led to a third law value of $\Delta H_f^{\circ}{}_{298} = 15 \pm 5$ Kcal. for the molecule BeCl(g). Greenbaum et.al.¹¹² studied the equilibrium of the reaction



in the region of 1573 - 1723° K by the molecular flow effusion technique. This gave $+ 3.7 \pm 3.8$ Kcal.mole⁻¹ for the heat of formation of BeCl(g) by the second law and the corresponding third law value was -2.0 ± 0.8 .

Spectroscopically determined values show a large variation in the dissociation energy of the gaseous molecule BeCl(g). Herzberg⁵³ calculated the D_0° as 4.2 e.v. Gaydon⁵⁴ obtained a value of 3.0 e.v. after applying correction for the ionic character of the BeCl(g) molecule. The measurements

of the bands by Novikov and Tunitskii¹¹³ yielded a value of 5.9 ± 0.5 e.v. for the dissociation energy of BeCl(g) . Corresponding values for the heat of formation of BeCl(g) are $+9.5^{53}$, $+37.1^{54}$ and -29.7 Kcal. mole⁻¹¹¹³ respectively. Since these values are widely varying an attempt has been made in the present study to determine the heat of formation of BeCl(g) .

5.2. APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus and general experimental procedure employed for the determination of the reaction of AlCl(g) with BeO(c) was the same as that used in the investigation of reaction of AlCl(g) with MgO(c) (Chapter 4). The BeO used in this work was of E. Merck grade, extra pure quality. It was briquetted at a pressure of 1200 kg./cm^2 and calcined. The briquettes were broken to a mesh size of 60 U.S. to give a large surface area which ensures complete equilibrium with the carrier gas. Beryllium oxide was placed in a passivated Kyanite boat which was contained in an alumina reaction tube of 1" I.D. The unloading of beryllium oxide after the reaction is quantitative and easy. The reaction tube was surrounded by a platinum wire wound tube furnace with three circuits giving a 11" constant temperature zone $\pm 7^\circ$. This was sufficient to accommodate two 5" long boats one for aluminium metal and the other for beryllium oxide. Temperatures were measured with a calibrated platinum-platinum 10% rhodium thermocouple. During the run the thermocouple was

positioned over the second boat and the temperatures were recorded. The average temperature in a 2-4 hours run was used for calculations. The variation of the temperature was not more than 10° . The average temperature of equilibrium zone was also checked at intervals.

The anhydrous aluminium chloride E. Merck grade, resublimed in an inert atmosphere before use was separately vaporized in a pyrex glass tube and allowed to pass over aluminium metal in the reaction tube. The AlCl_3 vaporization tube and alumina tube were connected through an adapter made of high purity high density graphite. The furnace surrounding the aluminium trichloride vaporization cell has a sliding arrangement, which helps to arrest the reaction quickly. Alumina shields ~~were~~ placed at the ends and in between the boats served as radiation shields and diffusion barriers. Spectrographically standard grade aluminium metal supplied by Johnson Mathey and Co. Ltd., London, was used to produce aluminium monochloride.

The general principles of the transpiration method employed here were described in detail in Chapter 2. In this method the carrier gas (argon) saturated with monochloride (90-95%) was allowed to react with BeO at atmospheric pressure. Flow rates around 100 cc/min. were used in the experiments where the effects of self and thermal diffusions were negligible (Chapter 3). After the experimental run of 2 to 4 hours the

and Moser and Messner. The apparatus described in the

methods was checked in few cases and was found good.

heating of aluminium chloride was stopped, the boats were pushed out of hot zone and cooled under a flow of inert gas. The amount of BeO taking part in the reaction was determined by the analysis of the residue in the boat.

X-ray and spectrographic methods were employed to identify the reaction products. The gaseous products condensed on cold parts were also examined. When the boat was weighed after cooling, it not only showed the increase in weight of the boat alone, but also showed in the oxide content. Aluminium metal was also observed in the boat. X-ray powder pattern of the residue gave evidence for the presence of BeO: Al_2O_3 phase, but no lines were found which are associated with Al_2O_3 as a separate crystalline phase. The identification was possible by comparing the pattern with ASTM index¹¹⁴. The values are tabulated in Table XIX.

5.3. ANALYSIS

After the run the residue was washed with warm dilute hydrochloric acid (1.25 N) filtered, dried (at 1000°) and weighed. The difference in weight was found to be due to aluminium metal which was also confirmed by the analysis of the acid extract. The dried residue was ground in a mortar to fine uniform particles. An aliquot of it was fused with potassium bisulphate. The fused mass was extracted with dilute hydrochloric acid and the extract was analysed for Al_2O_3 by the methods described by Kolthoff and Sandel¹¹⁵ and Moser and Niessner¹¹⁶. The agreement between the two methods was checked in few cases and was found good.

Table - XIX

Prominent x-ray diffraction lines of $\text{BeO}:\text{Al}_2\text{O}_3$

Time of exposure : 2 hours

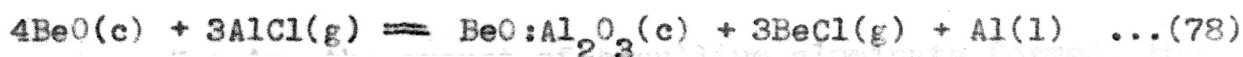
Radiation : $\text{Cu K}\alpha$

Nickel foil filter

Experimental		ASTM index for $\text{BeO}:\text{Al}_2\text{O}_3$		ASTM index for BeO	
$d^\circ \text{A}$	Relative intensity	$d^\circ \text{A}$	Relative intensity	$d^\circ \text{A}$	Relative intensity
4.0404	M	4.47	40	2.337	91
3.6361	M	3.60	50	2.061	100
		3.24	80	1.598	22
2.8412	W	2.85	40	1.349	29
2.5815	S	2.57	80	1.238	24
				1.1682	4
2.3374	S+	2.33	80	1.1482	16
2.2872	W	2.26	70	1.1287	5
2.1044	S++	2.08	100		
1.8110	W	1.98	20		
		1.88	20		
1.6294	S++	1.80	60		
		1.65	40		
1.5632	VW	1.61	100		
1.5230	W	1.56	20		
		1.51	50		
1.4813	W	1.46	50		
1.3749	M	1.36	80		
		1.34	40		
		1.30	70 _D		

Spectrographic analysis of the metal drops collected beyond the reaction zone, on the thermocouple sheath, showed the presence of beryllium and aluminium. The condensate when heated at 500° in an inert atmosphere gave off chlorides of beryllium and aluminium and the residue remained behind showed the presence of metals aluminium and beryllium. This suggests that beryllium might have disproportionated from BeCl(g) .

Considering $\text{BeO:Al}_2\text{O}_3(\text{c})$ and BeCl(g) as the products, the possible equilibrium reaction can be represented as



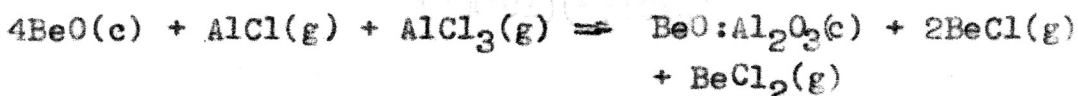
5.4. EFFECT OF ALUMINIUM TRICHLORIDE OVER THE REACTION

The results obtained by the transpiration experiments when calculated for the reaction (78), the second law plot of $\log K$ vs $1/T$ gave an intercept leading to a value of the entropy of the reaction which is 6 times greater than that which was calculated from the 'JANAF' tables⁸⁸. This might be due to the side reaction of aluminium trichloride with the products. In this work the amount of $\text{AlCl}_3(\text{g})$ present is only 10% in the AlCl(g) but it is sufficient to bring about the side reaction



Reaction (79) proceeds with positive entropy and the free energies are negative at these temperatures. Thus combining

reactions (78) and (79) the equilibrium reaction will be



The thermodynamic generalizations⁴³⁻⁴⁴ suggest that the above reaction is probable. When AlCl_3 was passed over BeO , the reaction was not as extensive as that with $\text{AlCl}(\text{g})$. It was also found that when aluminium metal was mixed with BeO , the aluminium trichloride reacted preferably with Al-metal and not with $\text{BeO}(\text{c})$.

5.5. TREATMENT OF THE DATA

Knowing the amount of beryllium aluminate formed, the beryllium oxide which took part in the reaction was determined and the equilibrium constant was calculated. The partial pressures of BeCl , BeCl_2 , AlCl and AlCl_3 were calculated from the weight loss data (BeO and Al) assuming that the ideal gas law holds good in the equilibrium zone.

$$P_{\text{BeCl}} = \frac{2}{4} n_{\text{BeO}} \frac{RT_r}{V_r} \quad \dots(80)$$

$$P_{\text{BeCl}_2} = \frac{1}{4} n_{\text{BeO}} \frac{RT_r}{V_r} \quad \dots(81)$$

$$P_{\text{AlCl}} = \left[\frac{\Delta W_{\text{Al}} \times 187.21}{53.96 \times 62.437} - \frac{2}{4} n_{\text{BeO}} \right] \frac{RT_r}{V_r} \quad \dots(82)$$

$$P_{\text{AlCl}_3} = \left[\frac{1}{133.35} \left(\Delta W_{\text{AlCl}_3} - \frac{\Delta W_{\text{Al}} \times 133.35}{53.96} \right) - \frac{1}{4} n_{\text{BeO}} \right] \frac{RT_r}{V_r} \quad \dots(83)$$

The equilibrium constant at a given temperature was calculated by the expression:

$$K_p = \frac{(P_{\text{BeCl}}^2)(P_{\text{BeCl}_2})}{(P_{\text{AlCl}})(P_{\text{AlCl}_3})} \quad \dots(84)$$

Experimental data and calculated equilibrium constants are given in Table XX.

5.6. RESULTS AND DISCUSSION

The free energies and the third law heat were calculated employing the following relations:

$$\Delta F_T = -RT \ln \frac{(P_{\text{BeCl}}^2)(P_{\text{BeCl}_2})}{(P_{\text{AlCl}})(P_{\text{AlCl}_3})} \quad \dots(85)$$

$$\Delta H_{298}^{\circ} = T \left[\frac{\Delta F_T^{\circ}}{T} - \Delta \frac{F_T^{\circ} - H_{T_{\text{ref}}}^{\circ}}{T} \right] \quad \dots(86)$$

The free energy functions for BeCl(g) , $\text{BeCl}_2(\text{g})$, AlCl(g) , $\text{AlCl}_3(\text{g})$ and BeO(c) were taken from the 'JANAF' tables⁸⁸. The thermal functions for $\text{BeO:Al}_2\text{O}_3$ crystal were taken from Ditmars and Douglas¹¹⁷. The third law calculations for the reaction (7) are given in table XXI.

A plot of the logarithm of the equilibrium constant of the reaction vs the reciprocal of the absolute temperature allows the determination of the heat of reaction, ΔH_r over the temperature range of investigation. Figure 8 represents the data in this form. The least squares analyses of the experimental data lead to an equation:

Table - XX

Experimental data for the reaction $4\text{BeO}(c) + \text{AlCl}(g) + \text{AlCl}_3(g) = \text{BeO}:\text{Al}_2\text{O}_3(c) + 2\text{BeCl}(g) + \text{BeCl}_2(g)$

$T^\circ \text{K}$	t, min	$\Delta W_{\text{Al}} \text{ g.}$	$\Delta W_{\text{BeO}}:$ $\text{Al}_2\text{O}_3 \text{ g.}$	$P_{\text{AlCl}} \text{ g.}$	$P_{\text{AlCl}} \text{ atm.}$	$P_{\text{AlCl}_3} \text{ atm.}$	$P_{\text{BeCl}} \text{ atm.}$	$P_{\text{BeCl}_2} \text{ atm.}$	K_p
1389	240	3.2957	0.5024	0.3217	1.7457 x 10 ⁻¹	1.5506 x 10 ⁻²	6.2398 x 10 ⁻³	3.1199 x 10 ⁻³	4.4871 x 10 ⁻⁵
1415	240	4.3654	0.6513	0.4899	2.4780 x 10 ⁻¹	1.6363 x 10 ⁻²	9.9774 x 10 ⁻³	4.9887 x 10 ⁻³	1.2248 x 10 ⁻⁴
1425	180	3.0625	0.3493	0.2343	2.3128 x 10 ⁻¹	2.4009 x 10 ⁻²	6.4922 x 10 ⁻³	3.2461 x 10 ⁻³	2.5640 x 10 ⁻⁵
1453	240	4.2553	0.6293	0.5220	2.4799 x 10 ⁻¹	1.6408 x 10 ⁻²	1.1190 x 10 ⁻²	5.5950 x 10 ⁻³	1.7218 x 10 ⁻⁴
1468	180	3.3294	0.5988	0.5403	2.4397 x 10 ⁻¹	1.3571 x 10 ⁻²	1.4672 x 10 ⁻²	7.3360 x 10 ⁻³	4.7697 x 10 ⁻⁴
1492	120	2.3698	0.4961	0.3956	2.6042 x 10 ⁻¹	1.2471 x 10 ⁻²	1.6114 x 10 ⁻²	8.0570 x 10 ⁻³	6.4417 x 10 ⁻⁴

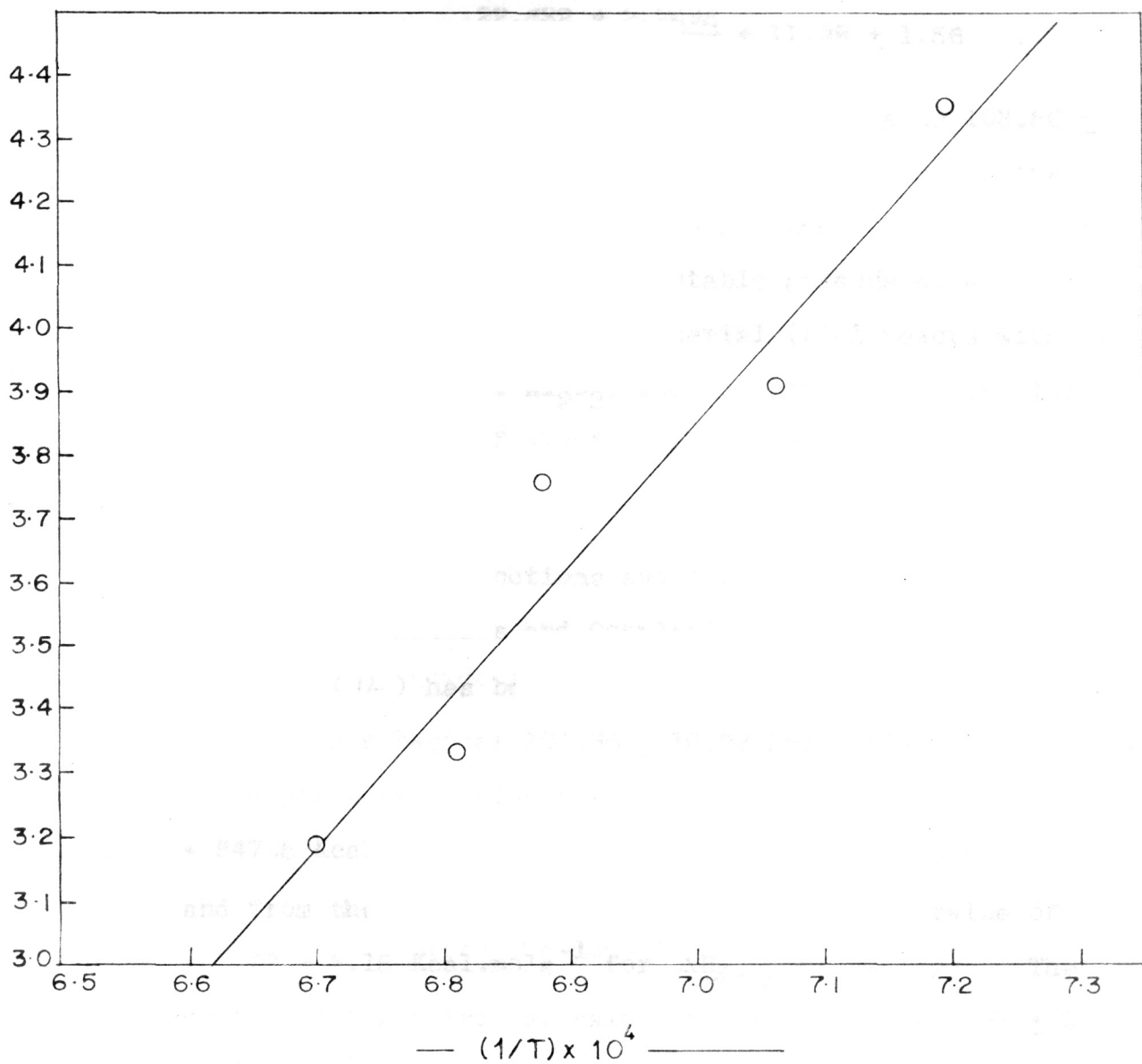


FIG. 8- EQUILIBRIUM CONSTANTS OF THE REACTION $4 \text{BeO}(c) + \text{AlCl}(g) + \text{AlCl}_3(g) \rightleftharpoons \text{BeO} \cdot \text{Al}_2\text{O}_3(c) + 2 \text{BeCl}(g) + \text{BeCl}_2(g)$ AS A FUNCTION OF TEMPERATURE

Table - XXI

Third law heats for the reaction $4\text{BeO}(\text{c}) + \text{AlCl}(\text{g}) + \text{AlCl}_3(\text{g})$
 $\quad\quad\quad = \text{BeO}:\text{Al}_2\text{O}_3(\text{c}) + 2\text{BeCl}(\text{g}) + \text{BeCl}_2(\text{g})$

$T^\circ\text{K}$	- Log K	- RlnK	- RTlnK	$-\frac{E_0^\circ}{T} - H_{298}$	ΔH_{298}	ΔH_{f298}
1389	4.3480	19.89 17.90	27.82	37.660	79.95	-5.13
1415	3.9119	17.90	25.33	37.634	78.58	-5.81
1425	4.5911	21.00	29.93	37.634	83.55	-3.33
1453	3.7643	17.23	25.04	37.618	79.69	-5.26
1468	3.3215	15.20	22.31	37.612	77.53	-6.33
1492	3.1920	14.61	21.80	37.584	77.87	-6.17
						Avr. -5.67
						$\pm$
						0.60

$$\log K = - \frac{22,532 + 2,2496}{T} + 11.98 \pm 1.56 \quad \dots(87)$$

The constants from the equation 15 give a value 103.56 ± 10.29 K cal. mole⁻¹ for the heat of formation over the experimental range. The fairly high least square standard deviation is largely due to unstable gaseous molecules reacting with the container material (AlCl reacts with BeO and BeCl reacts with Al₂O₃) and separation difficulties of the small amounts of alumina from beryllia encountered during the analyses.

From the functions available in the 'JANAF' tables⁸⁸ and those of Dittmars and Douglas¹¹⁷ the $\Delta(H_{1440} - H_{298}^O)$ for reaction (12) has been found to be $- 1.1$ Kcal.mole⁻¹. The ΔH_{298} thus becomes 104.66 ± 10.29 Kcal.mole⁻¹. Employing the experimental value for the heat of reaction, a value of $- 547.5$ Kcal.mole⁻¹ for ΔH_{f298} for the spinel BeO:Al₂O₃¹¹⁸ and from the values of the 'JANAF' tables⁸⁸ a value of $+ 7.23 \pm 5.15$ Kcal.mole⁻¹ for ΔH_{f298} of BeCl(g). The corresponding third law value for BeCl(g) is $- 5.67 \pm 0$ Kcal. mole⁻¹ is not in good agreement with that obtained from the second law. The deviation may be due to the temperature dependent errors coupled with inherent experimental difficulties as stated above. Apparently, there is no suitable container material for the study of this reaction. The amount of side reaction was less than 10% and the influence of this effect on experimental results was minimised when the data are obtained by analysis.

From the intercept the entropy of the reaction calculated was $54.83 \pm 7.14 \text{ cal.deg.}^{-1}$ for ΔS_{1440} which differs by $15 \text{ cal.deg.}^{-1} \text{ mole}^{-1}$ with that of the theoretical value calculated from the 'JANAF' tables⁸⁸.

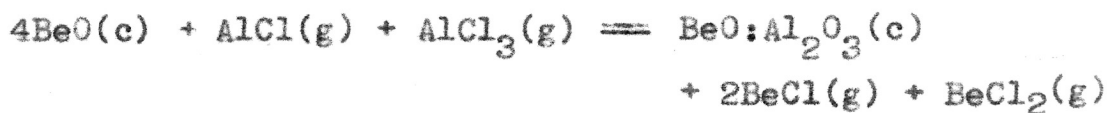
The third law treatment of the data gives the meaningful heat of formation ($\Delta H_{f,298} = -5.67 \pm 0.60 \text{ K.cal. mole}^{-1}$).

5.7. CONDENSATION

It is difficult to follow the individual species in a heterogeneous system where the products of the reaction are more than one gaseous species (viz. BeCl_2 and BeCl). In an attempt to condense the gaseous products of the reaction (12) a small mullite tube was inserted in the reaction zone. After the experiment the condensed material in the tube was chemically analysed and the presence of beryllium metal was noted. This confirms the formation of BeCl(g) . It was difficult to obtain the quantitative data in the condensation experiments due to the presence of large excess of AlCl(g) in the system.

Table - XXII

Thermodynamic data for the reaction



$$\text{Log } K = - \frac{22,632 \pm 2,249}{T} + 11.98 \pm 1.56$$

$$\Delta H_{1440}^{\circ} = 104.66 \pm 10.29 \text{ Kcal.mole}^{-1} \text{ (second law)}$$

$$\Delta H_{298} \text{ for BeCl(g)} = + 7.23 \pm 5.15 \text{ Kcal.mole}^{-1} \text{ (second law)}$$

$$\Delta H_{298} \text{ for BeCl(g)} = - 5.67 \pm 0.60 \text{ Kcal.mole}^{-1} \text{ (third law)}$$

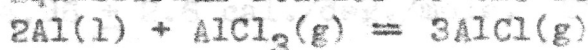
$$\Delta S_{1440} = 54.83 \pm 7.14 \text{ cal.deg.}^{-1} \text{ mole}^{-1}$$

S U M M A R Y

S U M M A R Y

Reactions involving light metals and their compounds were studied at high temperatures.

(1) Equilibrium studies of the reaction



The equilibrium reaction (1) was studied between 1125 and 1425°K, employing a transpiration technique.

Over the temperature range the ΔH_r was found to be 90.86 ± 1.6 Kcal/mole. The ΔS_r at 1275 was 60.12 ± 1.3 cal./deg./mole. From the available thermal functions the second law ΔH_r at 298 obtained was -12.45 ± 0.54 Kcal/mole which compared favourably with the third law value of -12.04 ± 0.22 Kcal/mole.

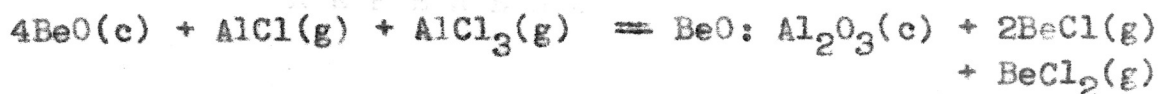
(2) Reaction of $\text{AlCl}(g)$ with $\text{MgO}(c)$ and the heat of formation of $\text{MgAl}_2\text{O}_4(c)$

The reaction of aluminium monochloride with magnesium oxide was investigated between 1298 and 1465°K employing a flow method. The products of the reaction and the weight loss measurements suggest that the equilibrium reaction was

$$4\text{MgO}(c) + 3\text{AlCl}(g) = \text{MgAl}_2\text{O}_4(c) + \text{AlCl}_3(g) + 3\text{Mg}(g)$$

The reaction yielded a third law heat, ΔH_r at 298 = 21.85 ± 0.84 Kcal/mole which compared favourably with the second law value of 24.03 ± 2.49 Kcal/mole. These values gave -553.36 ± 1.89 and -551.18 ± 3.55 Kcal/mole respectively

for the heat of formation of magnesium aluminate from the elements. The heat of formation of $\text{MgAl}_2\text{O}_4(\text{c})$ from the oxides at 298°K was found to be -9.26 ± 1.89 Kcal/mole from the third law and -7.08 ± 3.55 Kcal/mole from the second law. The ΔS_r over the temperature range studied was 14.96 ± 2.6 cal./deg./mole. The reaction of aluminium monochloride with magnesium aluminate was much less than that of the reaction with $\text{MgO}(\text{c})$. The reaction of aluminium monochloride with beryllium oxide was investigated between 1389°K and 1492°K employing the transpiration method. The analyses of the products of the reaction and the amount of $\text{BeO}(\text{c})$ reacted suggest that the equilibrium is:



Over the temperature range the ΔH_r was found to be 103.56 ± 10.29 Kcal/mole. From the recent experimental data and available thermal functions, the $\Delta H_{f,298}$ for $\text{BeCl}(\text{g})$ was found to be $+7.23 \pm 5.15$ Kcal/mole by the second law and the corresponding third law value was -5.67 ± 0.60 . The entropy of the reaction at 1440°K was 54.83 ± 7.14 cal./deg./mole which differs by 15 cal./deg./mole with that of the theoretical value.

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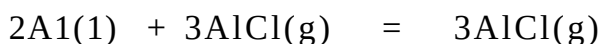
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A P P E N D I X

The work included in Chapter 3 has been published in the Journal of Physical Chemistry:

"The **equilibrium** studies of the reaction



D. Bhogeswara Rao and V. V. Dadape,
J. Phys. Chem., 70, 1349 (1966)."

The topic dealt in Chapter 4 has been accepted for publication in the Journal of Physical Chemistry:

"Reaction of $\text{AlCl}(\text{g})$ with $\text{MgO}(\text{c})$ and the heat of formation of $\text{MgAl}_2\text{O}_4(\text{c})$

D. Bhogeswara Rao and V. V. Dadape".

The results of the reaction involving $\text{BeO}(\text{c})$ and $\text{AlCl}(\text{g})$ (work described in Chapter 5) has been communicated.

Equilibrium Studies of the Reaction $2\text{Al(l)} + \text{AlCl}_3(\text{g}) \rightleftharpoons 3\text{AlCl(g)}$

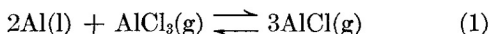
by D. Bhogswara Rao and V. V. Dadape

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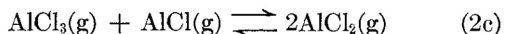
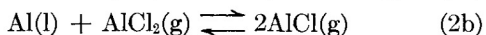
The equilibrium reaction $2\text{Al(l)} + \text{AlCl}_3(\text{g}) \rightleftharpoons 3\text{AlCl(g)}$ was studied between 1125 and 1425°K, employing a transpiration technique. Over the temperature range the ΔH_r was found to be 90.86 ± 1.6 kcal. The ΔS_{r1275} was 60.12 ± 1.3 cal deg⁻¹. From the available thermal functions the second-law ΔH_{f298} obtained was -12.57 ± 1.6 kcal mole⁻¹ for AlCl(g) , which compared favorably with the third-law value of -10.41 ± 0.22 kcal mole⁻¹.

Introduction

Ever since the vapor phase existence of monovalent chloride of aluminum was established by Bhaduri and Fowler,¹ the equilibrium reaction

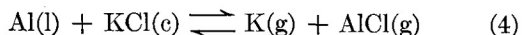
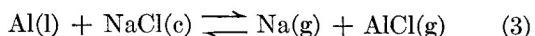


has been studied by several workers at high temperatures (the range being 880–1800°K). The chemical literature has a number of references to the heat of formation of the subhalide, but the values are not in good agreement with one another though similar techniques have been employed.^{2–5} Experimental values of Heimgartner⁴ disagree with the calculated ones, and consequently the equilibrium reaction (1) was rejected, and the following reactions were proposed



the $\text{AlCl}_2(\text{g})$ being considered as the main species. However, there is no evidence in the literature about the stability of $\text{AlCl}_2(\text{g})$ species at high temperatures. The ΔH_{f0} values of Weiss,² Russell, *et al.*,³ and Semenkovich⁵ were -17 , -10.7 , and -16 kcal mole⁻¹, respectively, for the molecule AlCl(g) .

The heat of formation ($\Delta H_{f0} = -10.7$ kcal) obtained from equilibrium studies by Russell, *et al.*,³ compared well with that deduced ($\Delta H_{f298} = -11.58$ kcal) by Gross, *et al.*⁶ However, in the latter work, the following reactions have been investigated in conjunction



with reaction 1. The ΔH_{f298} values of AlCl(g) from reactions 3 and 4 did not correspond with that obtained from reaction 1. The observed difference of more than 4 kcal in the free energy of reaction has been attributed to the unreliable thermochemical data for $\text{AlCl}_3(\text{g})$ and to the fact that the equilibrium might not have been reached during the experiment. In reaction 1, the matter appears to be complicated by the possibility of the formation of $\text{AlCl}_2(\text{g})$.⁴

Foster, *et al.*,⁷ and Heise and Wieland⁸ have calculated from spectroscopic measurements the ΔH_{f0} of AlCl(g) molecule giving the values -13.8 and -10.5 ± 2 kcal, respectively. Widely differing values of dissociation energies calculated from the spectra of diatomic molecules have been reported by Gaydon⁹ ($D^\circ_{298} = 117.6$ kcal) and Herzberg¹⁰ ($D^\circ_{298} = 71.5$ kcal.). The corresponding heats of formation ΔH_{f298} were -11.6 and $+34.5$ kcal mole⁻¹, respectively.

Considering the above discrepancies in the thermochemical data, the equilibrium reaction (1) has been

(1) B. N. Bhaduri and A. Fowler, *Proc. Roy. Soc. (London)*, **A145**, 321 (1934).

(2) P. Weiss, *Z. Erzbergbau Metallhuettenw.*, **3**, 241 (1950).

(3) A. S. Russell, *et al.*, *J. Am. Chem. Soc.*, **73**, 1466 (1951).

(4) R. Heimgartner, *Schweiz. Arch. Angew. Wiss. Tech.*, **18**, 241 (1952).

(5) S. A. Semenkovich, *Zh. Prikl. Khim.*, **33**, 1281 (1960); *J. Appl. Chem. USSR*, **33**, 1269 (1960).

(6) P. Gross, *et al.*, *Discussions Faraday Soc.*, **4**, 206 (1948).

(7) L. M. Foster, *et al.*, *J. Am. Chem. Soc.*, **72**, 2580 (1950).

(8) M. Heise and K. Wieland, *Helv. Chim. Acta*, **34**, 2182 (1951).

(9) A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall Ltd., London, 1953.

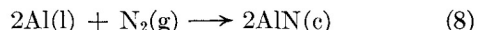
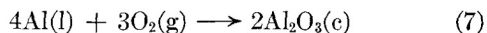
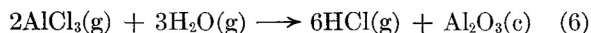
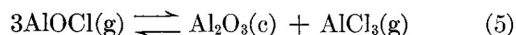
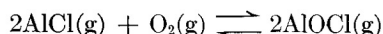
(10) G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1963.

studied at high temperatures (1125–1425°K) employing the transpiration technique, which has been reviewed by Margrave.¹¹ The studies have also been carried out in regard to the corrosive nature of the molecule $\text{AlCl}(\text{g})$.

Experimental Section

Materials. Aluminum wire having 99.98% purity (BDH AR quality) was melted in an argon atmosphere to expel the dissolved gases (if any), and the resulting ingot was cut into chips. These chips were degreased and used. Spectrographic analysis of the sample indicated that it contained trace impurities (nearly 200 ppm), *viz.* Fe, Cu, and Si. Aluminum chloride with 99.9% purity (E. Merck grade) was resublimed in an inert atmosphere before use. Resublimed product contained 0.04% ferric chloride and 0.02% alumina.

Purification of Argon. Argon was used as a carrier gas. It is necessary to purify argon, as the impurities like oxygen, nitrogen, and moisture will react with aluminum or with the monochloride or trichloride as given below, thus affecting the apparent concentrations.



The purification process used by Gross, *et al.*,⁶ served well during the present work. In addition, sodalite (sodalime containing a little manganic acid) was also used to remove carbon dioxide.

Apparatus and Procedure. The experimental setup to study the high-temperature reaction between aluminum and aluminum trichloride was essentially similar to that reported by Hildenbrand, *et al.*¹² It may be described as follows.

A Kyanite refractory tube 60 cm in length and 2 cm in internal diameter was introduced in a Kanthal-wound tube furnace which gave a constant-temperature zone ($\pm 3^\circ$) of 25-cm length at temperatures between 1125 and 1425°K. To maintain a constant power supply, the Kanthal heating elements were connected to the 230-v main source, through a voltage stabilizer. The constant-temperature zone was long enough to accommodate a Kyanite boat (length 15 cm, width 1.5 cm, and height 1.5 cm) containing a sample of aluminum metal. Sections of Pyrex glass tubing of suitable sizes were connected to either end of the reaction tube with a high-alumina refractory cement (Accocet-50) which helped to give cemented gas-tight joints. In the

Pyrex tube at the upstream end a glass boat containing anhydrous aluminum chloride was introduced. The temperature of the Pyrex glass section was maintained at $150 \pm 3^\circ$ to facilitate the transport of the halide by argon gas. From the downstream end a Kyanite thermocouple sheath entered the reaction tube and was positioned over the center of the refractory boat. Initially, a chromel–alumel thermocouple calibrated up to the melting point of copper (1083°) served to measure the temperature during the experiment. A flowmeter was employed to measure the rate of flow of argon, and arrangements were also made to collect the gas during the run.

The rate of passage of pure argon was brought up to the desired value, and the experiment was started. After running the experiment for a definite time, the boat containing aluminum metal was pushed out of the hot zone by a refractory rod. The heating of the reaction tube and the Pyrex tube was stopped. The system was allowed to cool in an argon atmosphere. The rate of transport of aluminum trichloride as a function of the temperature and the rate of flow of argon gas were previously determined by a series of experiments.

The vapor pressure of aluminum monochloride formed during the reaction at high temperatures was calculated from

$$\frac{P_a}{P_t} = \frac{P_a}{P_a + P_b + P_t} = \frac{n_a}{n_a + n_b + n_t} \quad (9)$$

where P_a = the partial pressure of $\text{AlCl}(\text{g})$, P_t = total pressure = 720 mm, n_a = number of moles of $\text{AlCl}(\text{g})$ formed, n_b = number of moles of unreacted $\text{AlCl}_3(\text{g})$, n_t = number of moles of argon collected during the run. In each run the amount of AlCl_3 passed and the amount of chemically transported aluminum were found out by weight loss measurements. A good agreement was noticed between the loss in weight of the boat and the AlCl_3 collected. Loss in weight of aluminum was also checked by chemical analysis of the residual aluminum.

Results

In the transpiration method it is necessary to determine the limits of the flow rates of the carrier gas which is saturated with the gaseous reaction products. This helps us to know the extent to which the experimental results are being influenced by diffusion transport. If an equilibrium between a gaseous phase and a condensed phase is established with negligible diffusion

(11) J. L. Margrave, "Physicochemical Measurements at High Temperatures," J. O. M. Bockris, J. L. White, and J. D. Mackenzie, Eds., Butterworth Scientific Publications Ltd., London, 1959, Chapter 10.

(12) D. L. Hildenbrand, *et al.*, *J. Chem. Phys.*, **39**, 1973 (1963).

effects, the amount of vapor transported per unit time varies linearly with the flow rate of the gas mixture.¹³

In the present experiment the transport of vapor is directly proportional to the loss in weight of metal aluminum, and hence it was studied at a reaction temperature of 1183°K by varying the flow rate of a carrier gas (containing AlCl_3 vapor) between 25 and 130 ml/min. When the weight loss data were plotted against the flow rates in the above range, the weight loss increased linearly up to the flow rate of 107 ml/min, thereby indicating that the flow gas was saturated with the gaseous reaction products. The curve on interpolation passed through the origin showing that the diffusion effects were negligible. The equilibrium constant calculated at each one of the flow rates between 25 and 107 ml/min agreed well ($\pm 2\%$), which suggests that within these limits the reaction is independent of the flow rate of the carrier gas.

In a few preliminary experiments it was observed that the refractory boat (weight of the boat, 16.1740 g) increased in weight at the end of a run of 2 hr. After each succeeding run, the increase in weight progressively reduced. The boat showed almost negligible (less than 0.04%) increase in weight, after a total reaction period of 16 hr. Blank experiments carried out with aluminum metal only or by transporting AlCl_3 vapor over an empty boat at 1183°K showed no perceptible increase in the weight of the boat. In addition to the attack of aluminum monochloride on the boat material, it was also observed that the inner surface of the Kaynite tube got covered with a thin layer of a black refractory material in the initial runs. To ensure complete passivation of the inner surface of the tube, a series of experiments was carried out by placing a number of boats containing aluminum metal throughout the length of the tube. Consistent results in the equilibrium studies could be obtained only after the two surfaces were passivated. A small amount of black shining product (containing 81–83% silica, 14–15% aluminum, and 2–2.5% iron) as a result of this attack was collected. The behavior of the material toward heat treatment and the reaction with aluminum monochloride vapor was studied. It did not show any loss in weight even after several hours of heating at about 1650°K, nor did it react with aluminum chloride vapor at 1300°K. Once the boat was covered with the film of the above black material, the equilibrium reaction between molten aluminum and aluminum chloride vapor could be studied over a wide temperature range (1125–1425°K) without any difficulty.

Treatment of the Data

In the study of the equilibrium reaction (1) over the

temperature range 1125–1425°K, the experimentally determined weight loss data of Al and $\text{AlCl}_3(\text{g})$ were converted to partial pressures of AlCl(g) . The equilibrium constant for reaction 1 was calculated by substituting the pressures into the expression

$$K = \frac{P_{\text{AlCl}}^3}{P_{\text{AlCl}_3}} \quad (10)$$

The free energy and heats of reaction at various temperatures were calculated employing the equations

$$\Delta F^\circ = -RT \ln K \quad (11)$$

$$\begin{aligned} \frac{\Delta H^\circ_{298}}{T} &= -R \ln K - \\ &\sum \frac{F^\circ_T - H^\circ_{298}}{T} (\text{products}) + \sum \frac{F^\circ_T - H^\circ_{298}}{T} (\text{reactants}) \end{aligned} \quad (12)$$

The free energy functions $(F^\circ_T - H^\circ_{298})/T$ for the products and the reactants were taken from the "JANAF Tables."¹⁴

Discussion

The experimental data for reaction 1 have been summarized in Table I. Employing the well-known van't Hoff equation

$$(d \ln K)/d(1/T) = -(\Delta H/R) \quad (13)$$

the heat of reaction, ΔH_r , has been determined from the plot of the logarithm of the equilibrium constant *vs.* the reciprocal of the absolute temperature (Figure 1). The slope of the line obtained by the method of least squares gave the heat of reaction $\Delta H_r = 90.86 \pm 1.6$ kcal. This value of ΔH_r represents the mean value over the temperature range studied and does not take into account the effect of ΔC_p . From the functions cited in the "JANAF Tables,"¹⁴ $\Delta(H_{1275} - H_{298})$ for reaction 1 has been found to be -6.34 kcal. ΔH_{r298} thus becomes 97.20 ± 1.6 kcal, and its deviation from the third-law heat (103.69) may be due to the temperature-dependent errors which contribute significantly to the second-law calculations. The second-law heat of reaction thus permits the heat of formation of AlCl(g) to be calculated from the equation

$$\Delta H_{f298}\text{AlCl(g)} = \frac{1}{3}[\Delta H_{r298} + \Delta H_{f298}\text{AlCl}_3(\text{g}) + \Delta H_{f298}2\text{Al(l)}] \quad (14)$$

as -12.57 ± 1.6 kcal mole⁻¹, and the corresponding third-law value gives -10.41 ± 0.23 kcal mole⁻¹. The

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

(14) "JANAF Thermochemical Tables," revised ed, The Dow Chemical Co., Midland, Mich., 1964.

Table I: Transpiration Data and Related Third-Law Heats for the Reaction $2\text{Al(l)} + \text{AlCl}_3(\text{g}) \rightleftharpoons 3\text{AlCl(g)}^a$

Temp, °K	No. of moles of argon passed	AlCl ₃ passed, g	Loss in Al wt, g	P _{AlCl} , atm	Log K	-RT ln K	ΔH _{f298}	ΔH _{f298}
1125	0.5358	10.6495	0.1695	0.0144	-4.5839	23.5969	103.69	-10.40
1183	0.3247	10.8900	0.2495	0.0319	-3.7350	20.2011	103.49	-10.47
1183	0.5358	10.7477	0.3929	0.0324	-3.6622	19.8241	103.88	-10.34
1220	0.5464	10.9053	0.5630	0.0457	-3.0368	16.9529	103.00	-10.63
1225	0.5258	10.4902	0.5335	0.0450	-3.0584	17.1434	103.38	-10.51
1270	0.5464	10.9578	0.8417	0.0672	-2.4993	14.5251	103.53	-10.46
1280	0.5358	10.7626	0.8340	0.0679	-2.4850	14.5548	104.18	-10.24
1336	0.5154	10.8912	1.3324	0.1084	-1.8157	11.0998	104.11	-10.26
1373	0.5358	11.5390	1.9512	0.1479	-1.3270	8.3370	103.60	-10.43
1420	0.4958	10.7429	2.4808	0.1955	-0.8173	5.3085	103.46	-10.48
1425	0.5358	10.9600	2.4695	0.1834	-0.8972	5.8497	104.29	-10.20

Av -10.41 ± 0.22
kcal

^a Duration of each run is 2 hr.

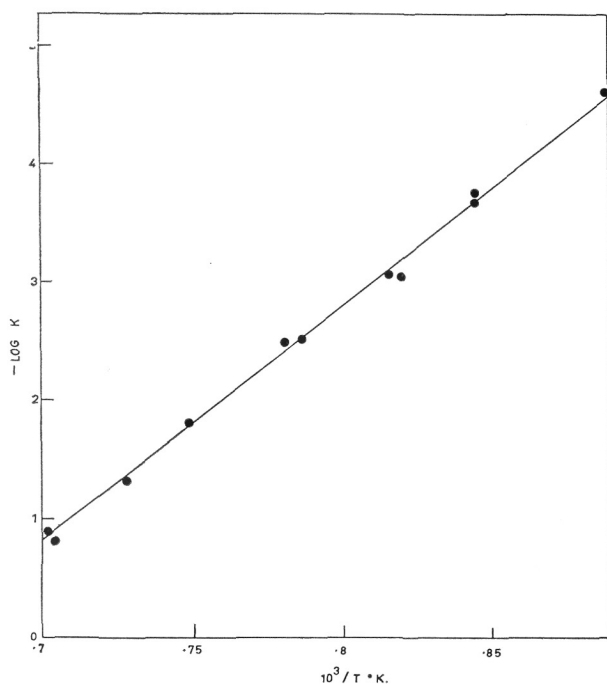


Figure 1. Plot of log K vs. $(1/T)$ from transpiration studies of the reaction $2\text{Al(l)} + \text{AlCl}_3(\text{g}) \rightleftharpoons 3\text{AlCl(g)}$.

uncertainties reported in this work are only those due to the statistical analysis of the data. The ΔH_{f298} for AlCl_3 and the heat of fusion for Al have been taken from the "JANAF Tables."¹⁴ To facilitate comparison, log K values at different temperatures reported by several workers have been recorded in Table II.

Table II: Comparison of the Values for Equilibrium Constants (log K)

Temp, °K				Ref
1000	1100	1300	1500	
Log K				
-7.1	-5.3	-2.5	-0.4	3
-5.3	-4.8	-1.4	0.3	5
-6.94	-5.09	-2.25	-0.17	6
-5.5	-3.8	-1.1	-0.9	7
-7.1	-5.2	-2.4	-0.4	8
-6.76	-4.96	-2.18	-0.14	Present work

The entropy of reaction ΔS_r is obtained from the second law of thermodynamics

$$\Delta F_r = \Delta H_r - T\Delta S_r \quad (15)$$

Employing the values of ΔF_r and ΔH_r at 1275°K, a value of $60.12 \pm 1.3 \text{ cal deg}^{-1}$ for ΔS_{r1275} is obtained. This value agrees well with the theoretical value of $\Delta S_{r1275} = 60.5 \text{ cal deg}^{-1}$ reported by Heimgartner⁴ and also agrees well with $\Delta S_{r1275} = 61.26 \text{ cal deg}^{-1}$ calculated from the data given in the "JANAF Tables."¹⁴ This good agreement suggests that the entropy of $\text{AlCl}_3(\text{g})$ at elevated temperatures may have considerable validity. The results of the present work are in very good agreement with those reported by Gross, *et al.*,⁶ as can be seen from Table II. It also shows that the presence of AlCl_2 species (as suggested by Heimgartner⁴) is not important in the temperature range studied.

While this manuscript was under the process of reviewing, the study of reaction 1 by Frisch, *et al.*,¹⁵ appeared, employing the molecular flow effusion technique over the temperature range 930–1034°K. An excellent agreement has been noted between their data and that of the present work. These authors have also derived the entropy of $\text{AlCl}_3\text{(g)}$ from the entropy of reaction 1 and the value of S°_{982} for $\text{AlCl}_3\text{(g)}$ is essentially 4 cal/deg/mole higher than the estimated value.¹⁵ Their value of $\Delta S^\circ_{982} = 55.1 \pm 1.1$ cal/deg mole differs by 5.0 cal/deg mole from the value calculated from "JANAF Thermochemical Tables." They have also concluded that the value of S°_{298} for $\text{AlCl}_3\text{(g)}$ as given in the "JANAF" tables is uncertain by at least 2 cal/deg mole.

The $\Delta S^\circ_{1275} = 60.12 \pm 1.3$ cal/deg reported in the

present work agrees well with the calculated value using "JANAF" tables and the difference was within the stated uncertainties. However, there is a difference of 6.5 kcal between the second-law and the third-law heats of reaction. The second-law heat may be in error due to the uncertainties in the thermodynamic functions of $\text{AlCl}_3\text{(g)}$, particularly in the reduction to 298°K. A revision, therefore, of these functions of $\text{AlCl}_3\text{(g)}$ may be of great help.

Acknowledgment. The authors wish to thank the Council of Scientific and Industrial Research for the award of a Junior Research Fellowship to D. B. R., which made possible the execution of this work.

(15) M. A. Frisch, M. A. Greenbaum, and M. Farber, *J. Phys. Chem.*, **69**, 3001 (1965).