STUDIES IN HIGH TEMPERATURE CHEMICAL REACTIONS INVOLVING METAL–METAL HALIDES AND METAL OXIDES–METAL HALIDES

BY

B. RADHAKRISHNA MURTHY, M.Sc.

A THESIS SUBMITTED TO
THE UNIVERSITY OF POONA
FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

MAY, 1970.

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(B. RADHAKRISHNA MURTHY)

CONTENTS

Page No:

CHAPTER – II

CHAPTER – III

SCOPE OF THE THESIS

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Study of chemical transport reactions is important for understanding

(A) the formation of subhalides with the same or different metals,

(B) the formation of spinels and oxyhalides when they (metal-halides) react with metallic oxides, and

(C) the thermodynamic properties of the species involved.

The present work aims at the study of the reactions at high temperatures involving subhalide and oxyhalide species such as MnCl(g) and AlOCl(g) respectively employing the transpiration technique.

No experimental data is available in the literature for the heat of formation of MnCl(g). Nevertheless one can calculate it from the dissociation energy of MnCl(g) molecule given by Herzberg and Gaydon. The values for ΔH_f thus obtained are 19.84 Kcal.(Herzberg), 26.74 ± 23 Kcal.(Gaydon) and 10.37 (Bulewicz). It is evident from these values that there is considerable discrepancy and hence it was thought worthwhile to carry out the present work.

Solid AlOCl has been reported by Schäfer *et.al.* in their study of the interaction of aluminium chloride with metallic oxides. Fischer found AlOCl(g) as one of the products of the reaction of alumina with chlorine at 1250°C. The existence of gaseous AlOCl at 2400°K has been reported by Greenbaum *et.al.* who claim to be the first to determine its heat of formation experimentally using the molecular effusion method in the study of the reaction

$$\frac{1}{3}Al_2O_3(l) + \frac{1}{3}AlCl_3(g) = AlOCl(g)$$

Apart from these few references in the literature, thermodynamic studies on AlOCl(g) have not been reported. Therefore, in the present work, an attempt has been made to study experimentally, by means of the transpiration technique, the reactions of some metal oxides with $AlCl_3$, AlOCl(g) being one of the products of the reaction.

The studies comprise the following:

(I) *Reactions of metal with halide*

(a) Equilibrium study of the reaction

$$Mn(c) + MnCl_2(g) \rightleftharpoons 2MnCl(g)$$

has been carried out at high temperatures to determine the heat of reaction, entropy of reaction and the heat of formation of MnCl(g). The experimental work is described in Section 2, Chapter II.

(b) Study of the reaction

$$2Mn(c) + AlCl_3(g) = MnCl_2(g) + MnCl(g) + Al(l)$$

has enabled us to determine the heat and entropy of reaction and the heat of formation of MnCl(g). The results of this work are included in Section 3, Chapter II.

(II) Reaction of metal oxides with halide

Reaction of $AlCl_3(g)$ with oxides of manganese, cobalt and iron have been studied at high temperatures. The reactions can be represented as follows:

$$Mn_3O_4(c) + 3.5AlCl_3(g) = \frac{1}{2}Al_2O_3(c) + 2.5AlOCl(g) + 3MnCl_2(g) + Cl_2(g)$$

$$6CoO(c) + 4AlCl_3(g) = CoAl_2O_4(c) + 2AlOCl(g) + 5CoCl_2(g)$$

$$2Fe_2O_3(c) + 5AlCl_3(g) = Al_2O_3(c) + 3AlOCl(g) + 4FeCl_3(g)$$

The experimental results are recorded in Sections 1, 2 and 3, Chapter III respectively. The data obtained was employed to calculate heat and entropy of reactions and the heat of formation of AlOCl(g).

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CHAPTER - I

INTRODUCTION AND THERMODYNAMIC CONSIDERATIONS

INTRODUCTION

1.1. SECTION - 1

1.1.1. GENERAL

High temperature chemistry is defined[1] as the chemistry of systems at sufficiently high temperatures so that the oxidation states, compounds and general chemical behaviour differ appreciably from those at room temperatures. During the past two decades, there has been a broad development of methods for measuring and attaining high temperatures, for studying the kinetics of high temperature reactions, for the determination of structural parameters of high temperature species, and for practical high temperature syntheses. High temperatures can be produced by several methods, viz. electrical resistance, flames, arcs and discharges, plasma jets, shock waves, etc. Extremely high temperatures (of the order of 10^6 to 10^8 °K) are produced by atomic fission and nuclear fusion. Employing chemical reactions[2], temperatures upto 6000°K can be obtained. The concentration of species with highly endothermic heats of formation will show rapid increase with rising temperature. Thus unstable molecules with little probability of forming at low temperatures, may become significant at high temperatures. Mass spectrography and optical spectra have given spectacular results in identifying the gaseous species at high temperatures. Some of the important radicals identified are: $(CH_3)_2N$, CS, CCl_2, CS_2, AlCl, AlF, BeCl, BeF, $(BOCl)_3$, BeC_2, LaC_2, Ca_2C_2, BeOH, $Si(OH)_4$, Al_2O, AlO, ZrO, B_2O_2, SiO, Al_2C_2, C_2, C_3, TiO, MgF, SrF, CaH, CO, CN, OH, O, H, N, NH_2, CF, MnCl, NiCl and CF_2. Because such unusual species are often observed and because reaction rates are also fast, Searcy[3] has suggested some descriptive laws of high temperature chemistry. At high temperatures, everything reacts with everything else, and the higher the temperature the more seriously everything reacts with everything else.

1.1.2. IMPORTANT HIGH TEMPERATURE REACTIONS

The significance of high temperatures is apparent when considered in terms of the second law of thermodynamics, in which the role of discrete particles and quanta in the conversion of energy from one form to another is examined. One of the most noteworthy achievements is the successful laboratory conversion of graphite and hydrocarbons to diamond by application of high temperature and high pressure. High temperatures play an important role in new chemical syntheses for mica, garnet and hornblende. Some of the important commercial high temperature thermal energy applications are in the following:

A) Calcium carbide production.
B) Silicon carbide production.
C) Boron carbide production.
D) Graphite production.
E) Aluminium production.
F) Magnesium production.
G) Petroleum processing.

The efficiencies of these processes in many cases will be higher if they are operated at still higher temperatures.

High temperature reactions are of importance in hydrothermal synthesis[4-8] and in geological processes[9].

1.1.3. CHEMICAL TRANSPORT REACTIONS

Possibilities for the production of new and unusual materials depend directly on the existence of unusual species which can act as intermediates at high temperatures. There are two ways of obtaining such important 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, ZrO, TiO, C_2, C_3, CN, Ba_2O, Ba_2O_2, BeO, B_2O_2, etc.

(B) By condensed phase or solid-liquid interactions e.g. metal-metal halide, metal halide-metal oxide, in which the species are MnCl, NiCl, AlCl, AlOCl, AlF, Al_2O, BeCl, BF, etc.

Definition of chemical transport

Chemical transport reactions are those in which a solid or liquid substance 'A' reacts with a gas to form exclusively vapour phase reaction products, which, in turn, undergo the reverse reaction at a different place in the system, resulting in the reformation of 'A'. Substance 'A', however, does not possess any appreciable vapour pressure at the applied temperatures. The substance is transported chemically e.g. when manganese chloride vapour is passed over metallic manganese, the equilibrium approached in the hot zone is

$$Mn(c) + MnCl_2(g) \rightleftharpoons 2MnCl(g) \qquad ...(1)$$

and reverts on cooling to manganese and its normal halide. However, solid and liquid interactions can also give unstable vapour phase compounds e.g. $Al_2O(g)$[10]

$$Al_2O_3(c) + Si(l) = SiO_2(c) + Al_2O(g) \qquad ...(2)$$

Schäfer[11] named this type of heterogeneous reactions as chemical transport reactions.

1.1.4. IMPORTANCE AND APPLICATIONS

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

By means of transport experiments one can prove whether or not suspected gaseous compounds actually exist. Furthermore, the unexpected transport of a substance can give indications of the existence of new compounds. Transport phenomena gave the first indications of the existence of aluminium(I) halides, silicon(II) halides and beryllium(I) hydroxide.

(A) In solid state reactions

Reactions between the starting solid materials can be enhanced when solid substances are joined together by a transport reaction. It is interesting to note that in a whole series of reactions with solids as starting materials, it has been shown that a liquid or gas phase is evolved as a reaction promoter[12], viz. the reaction between calcium and stannic oxides proceeds very rapidly when reducing agents such as H_2, CO and C are added[13,14].

$$2CaO(c) + SnO_2(c) = Ca_2SnO_4(c) \qquad \ldots(3)$$

$$SrO(c) + SnO_2(c) = SrSnO_3(c) \qquad \ldots(4)$$

In this system, the starting material need not be in contact with each other[13,15], since SnO_2 will be transported to the alkaline earth oxide via gaseous SnO

$$SnO_2(c) + CO(g) = SnO(g) + CO_2(g) \quad ...(5)$$

$$SnO_2(c) + H_2(g) = SnO(g) + H_2O(g) \quad ....(6)$$

(B) One of the most important recent chemical transport reactions is the formation of aluminium carbide by the action of aluminium monochloride on carbon[16]

$$2Al(l) + AlCl_3(g) = 3AlCl(g) \quad ...(7)$$

$$6AlCl(g) + 3C(c) = Al_4C_3 + 2AlCl_3(g) \quad ...(8)$$

Heim[16] has not only prepared Al_4C_3 at temperatures 900-1300°C by the above method, but also obtained it 95.8% pure.

(C) Chemical transport reactions are also useful in preparing spinels viz. $NiCr_2O_4$[17], $MgCr_2O_4$[18], $MgAl_2O_4$[19], etc. The formation of cobalt aluminate ($CoAl_2O_4$) through aluminium trichloride and cobalt oxide has been described in this thesis (Chapter III, Section 2).

(D) Mond-Longer process

This process utilises the reversibility of the reaction

$$Ni + 4CO = Ni(CO)_4(g) \quad ...(9)$$

for the preparation of pure nickel[20]. Finely powdered crude nickel is treated with carbon monoxide at 45 to 50°C.

The nickel carbonyl later decomposes to pure granular nickel.

(E) The iodide method developed by Van Arkel[21] is very useful for the purification of metals. In this the crude metal is vapourized as iodide and is decomposed on a hot wire[22]

$$Zr(C) + 2I_2(g) = ZrI_4(g) \qquad ...(10)$$

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

(F) Under suitable conditions metals like iridium[23], platinum[24] and silver[25] can be removed and pure crystals can be grown by transporting them through a stream of oxygen.

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

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

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

It is also possible to transport ruthenium, rhodium and palladium[26-28] in chlorine atmosphere.

1.1.5. ADVANTAGES OF TRANSPORT REACTIONS

(A) In the presence of a transporting gas phase, reactions may be carried out at considerably low temperatures viz. direct combination of aluminium and carbon gives aluminium carbide only at 1700-1800°C, but the formation of carbide takes place at much lower temperatures (900-1300°C) according to equation 8.

(B) Solid starting materials can be made to react even when they are not in contact. Consequently, it is not necessary to use stoichiometric primary mixtures. Quantitative analysis of the reaction products provides information which may lead to the elucidation of the reaction mechanism.

(C) Experimental procedures can be varied so that starting materials in the form of a powdered mixture can be used and the constituent in excess can be removed by a transport reaction after the conversion is completed. Thus the technique will be simple and the products will have high purity.

(D) The components of the reaction need not be mixed since one of them can be transported[13,15].

SECTION - 2

1.2. THERMODYNAMIC CONSIDERATIONS

1.2.1. THERMODYNAMIC STUDY

The main purpose of chemical thermodynamics is to predict chemical equilibria from the thermal data. The behaviour of chemical systems at high temperatures requires a detailed knowledge of thermodynamic properties of all solids, liquids and gases involved. Thus the application of thermodynamic methods to systems at high temperatures requires (i) identification of all species and phases present, (ii) determination of crystal structures, molecular geometry and vibrational, rotational and electronic energy levels, (iii) determination of heats of formation, and (iv) measurement of equilibrium constants and heat capacities over wide ranges of temperature and pressure. From such data one can then compute the equilibrium concentrations of species present at any temperature and decide on the feasibility of a given reaction.

Thermodynamic study of high temperature reactions is based on the measurement of the equilibrium pressures of the reaction. The study of vapo~~u~~rization process helps to establish the nature and energetics of chemical binding in the gaseous state.

Gilles[29] has rightly emphasised the importance of the following points in the study of high temperature chemical reactions.

(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.

1.2.2. GENERALIZATIONS USEFUL IN HIGH TEMPERATURE REACTIONS

The following three generalizations are helpful in predicting the gaseous products of an equilibrium reaction at high temperature. The first two are given by Brewer[30] and the third by Searcy[31,32].

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

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

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

1.2.3. METHODS FOR THE STUDY OF EQUILIBRIUM OF A REACTION

Experimental techniques for measuring the equilibrium vapour pressures directly and indirectly are described in detail by Margrave[33,34], Nesmeyanov[35] and Cooper and Stranks[36].

Vapour pressure - Its definition and usefulness

The vapour pressure of a substance is defined as the pressure of vapour in equilibrium with its condensed phase at a given temperature. The temperature variation of vapour pressure enables the heats of vapourization and sublimation to be evaluated. These heats are essential in calculating heats of formation, reaction and bond dissociation.

Vapour pressures by static or direct measurements

In the static methods, equilibrium pressures are measured in a closed vessel with the aid of measuring instruments such as mercury, ionization, spiral membrane or other type of manometers (direct method) or by measuring the quantity of the substance in a known volume (indirect method). Vapour density methods, sickle gauges, dew point method and boiling point method, are a few of the techniques for measuring vapour pressures directly. But in equilibrium reactions of the type $Mn(c) + MnCl_2(g) \rightleftharpoons 2MnCl(g)$ it is difficult to determine the vapour pressures by these methods due to the reactivity of the outgoing gases.

Indirect measurement of vapour pressures

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

Langmüir free evaporation [37-39]

This method is based on the determination of the rate of evaporation of the sample from an open surface in a vacuum. The vapour and the condensed phase are in dynamic equilibrium. The disadvantage in this method is that the pressure measured is not necessarily the equilibrium vapour pressure and that the vapour species must be identified independently.

Knüdsen effusion method

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

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

$$P = \frac{1}{A_o} \frac{dw}{dt} \sqrt{2\pi KT/m} \qquad ...(14)$$

Though a large number of thermodynamic data at high temperatures has been obtained by this method, many of its aspects viz. the correction to be applied to the shape of the crucible and the effusion hole, the effect of the location of the evaporating surface, the distribution of molecular velocities in the beam and the upper pressure limit at which the method is suitable are not clear. These problems have been discussed in detail in the literature[29,40-43]. Apart from the above points, the method has only a limited scope for the study of equilibrium pressures of a reaction involving corrosive species because of the following reasons.

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

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

The Torsion effusion method

In this method the sample is placed in an effusion cell suspended by a fiber. The cell contains two holes at opposite sides displaced in opposite directions from the centre.

The vapour effusing through the holes causes a torque on the cell and the rotational displacement of the cell is measured by a mirror attached to the suspension. This method has received a good deal of attention because of the speed with which the vapour pressure can be obtained in the direct determination of the molecular weight of the effusing species. Searcy and Freeman[43,44] have used this technique to study a number of organic and inorganic systems.

Molecular flow effusion method

The molecular flow effusion method has been developed and worked during recent years by De Marcus[45], Whitman(1953)[46], Modzfeldt(1955)[47], Balson(1961)[48] and Farber(1962-66)[49]. This method involves an impinging gas at the temperature of the reaction striking the reacting material at pressures allowing molecular flow. The concentration of the molecular constituents is determined by the equilibrium constant, employing the Knüdsen equation

$$n = p/(2\pi mkt)^{1/2} \qquad \ldots(15)$$

n = number of moles striking the surface.

Optical spectroscopy

None of the experimental methods described above enables us to determine the structure and thermodynamic properties of the gases produced in vapo~~u~~rization reactions.

Optical spectroscopy makes possible the determination of molecular configurations and electronic, vibrational and rotational energy levels. Thus spectroscopy provides the data for computation of thermodynamic properties by statistical mechanical methods.

Isotopic exchange method[50-52]

The principle of the method requires measurement of the rate of isotopic exchange between two samples of the substance under study. The two samples chemically identical but different in isotopic composition are placed in vacuum side by side at constant temperature. The atoms that escape from the surface of one sample fall on the surface of the other sample and vice versa. Thus a continuous exchange of atoms occurs between the two surfaces. It is assumed that all the atoms which strike the surface of the samples condense.

The change in specific activity due to the changes in the isotopic composition of the substance depends on the rate of evaporation(n_o), on the rate of self diffusion which is described by the coefficient of self diffusion (D), on time (t) and on the specific activity of the surface of the opposite sample (μ_1 or μ_2 respectively).

$$\text{Thus } \mu_1 = f(\mu_2, n_o, D, t)_T = \text{Constant} \qquad \ldots(16)$$

$$\mu_2 = f(\mu_1, n_o, D, t)_T = \text{Constant} \qquad \ldots(17)$$

where T is the temperature.

Solving this system of equations for n_o makes it possible to determine the pressure of the saturated vapour as μ_1 and μ_2 change with time at constant temperature.

Mass spectrometric method

This method which has been very useful to determine the composition of the gas phase consists of the ionization of the vapour of substances by means of electrons and identification of the ions formed.

Chupka and Inghram[53-55] constructed a mass spectrometer, one of the specialities of which is the use of a well focussed molecular beam which passes through an ionization chamber. In this apparatus, the vapour of the sample being studied cannot react with the material of the walls of the ionization chamber or with the material that serves as a source of electrons. The increased sensitivity of the apparatus makes it possible to use ionizing electrons with an energy of only a few electron volts. This reduces the possibility of disrupting the molecules.

This method has been widely used for studying the composition of vapours and for determining the partial pressures of many substances such as carbon[56], silver[57,58], germanium[59] and others[60-62].

1.2.4. FLOW, TRANSPIRATION OR TRANSPORTATION METHOD

The most important method for measuring vapour pressures greater than 10^{-3} atms. is the flow or transpiration method first used by Regnault[63] and Vonwartenberg[64]. Excellent reviews by Kubaschewski and Evans[65], Margrave[33], Richardson and Alocock[66] and Schäfer[11], are available in the literature giving applications of the method and the descriptions of many experimental techniques employed in this field.

This method deals with the measurement of transport of the material under study. The transport of a substance may be due to appreciable vapo~~u~~rization of the samp~~e~~l at that temperature or may be due to a gas, inert or reactive being passed over a condensed sample at a rate sufficiently low for equilibrium conditions to be established. The gas is collected at some point downstream from the sample and is analyzed to determine the vapour and dissociation pressures of components in the sample.

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

$$a\,A(s \text{ or } l) + b\,B(g) = cC(g) \qquad \ldots(18)$$

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

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

$$\frac{P}{P_T} = \frac{P}{P+P_f} = \frac{n}{n+n_f} \qquad \ldots(19)$$

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

Importance of equilibrium in transport study

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

(1) All the reagents participating in the reaction must be at the equilibrium temperature. This will be facilitated by preheating the gases before they enter the reaction zone.

(2) The pressure of the equilibrium zone must be the same as that of the entire flow system. Temperature and pressure gradient causes the reverse reaction to occur i.e. the reformation of solid reactants.

(3) The reaction zone must attain equilibrium and remain undisturbed during the transport period.

(4) In order to maintain the equilibrium, the carrier gas must be pure and dry. For e.g. in Mn-$MnCl_2$ system, if the carrier gas contains appreciable amounts of O_2, air or

water vapour, they will react with Mn or $MnCl_2$ with the formation of oxides, thus hindering the reaction and giving much lower transport of manganese.

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

(6) Flow rate should be measured accurately.

(7) Side reactions between sample and container or flow gas or product, with the reaction tube should be avoided. Very few refractory materials are useful for molten metals.

For equilibrium measurements, it is therefore necessary to test the materials for which the free energy change for a simpler reduction by the liquid metal has a large positive value. If extensive contamination or reaction occurs, the materials should be brought to equilibrium with the liquid metal or reactive species, so that it is saturated with respect to the solution, either of the metal itself or of the products of the reaction between metal and refractory material. This will minimize the attack or the container will be passivated.

Saturation of a carrier gas

The flow or carrier gas should be saturated with vapour. The establishment of the saturation flow is the most important factor in achieving equilibrium. The equilibrium flow rate is different for every system and also dependent on the construction of the apparatus. For tubes of 1 to 2.5 cm. in diameter which were used in the present study, gas flows from 2-10 litres per hour (20°C, 1 atm.) have usually proved to be satisfactory.

High flow rates can be used if the chemical reaction attains equilibrium rapidly. In the high temperature system in which equilibrium is not rapidly attained, diffusion rather than a chemical reaction is usually the rate determining step. Such diffusion processes require longer temperature zones, larger surface area of the sample and slow flow rates. If the flow rate is too high, the carrier gas will not be saturated and the apparent pressures will be low. If the carrier gas velocity is too low, sample may be transported due to the self-diffusion and thermal diffusion. It is, therefore, essential to establish the saturation flow rates where the vapour pressure is independent of flow rate.

If an unsaturated flow gas is suspected a series of experiments at various flow rates should be carried out until a range of flow rate is found for which the mass of sample transported per unit volume of flow gas remains constant. Thus a plot of (n_v/n_c) (mass of the sample transported per unit volume) vs n_f should approach a plateau region for n_f values where saturation is complete. For unsaturated flow this plot will not level off. This has been discussed by Lapore and Van Wazer[67]. 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, the amount of vapour transported per unit time varies with the flow rate of gas mixture[68]. However, it can be shown that at sufficiently high flow rates, diffusion effects become negligible. Diffusion occurs when rate of flow is too slow and the apparent pressures will be too high. Merten[68,26] has derived the equation

$$P = \frac{m}{t_v} \frac{RT}{M} \left[1 - \exp \left(- \frac{vt}{DA} \right) \right] \qquad \ldots(20)$$

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

$$P = (m/t.V)(R\ T/M) \qquad \ldots(21)$$

He has also pointed out that the equation may be used to obtain not only the pressure but also diffusion coefficient in favourable cases. Ackerman <u>et.al</u>.[69] have confirmed the validity of this equation. According to Merten[68,26], reliable pressures can be calculated if experimental determinations are available at two significantly different flow rates for which saturation has been reached.

Advantages of transport method

The significance of this technique is brought out in the case of silicon transport in the reaction of Si with $SiCl_4$[70-72]. By using the flow method Schäfer[70] has transported considerable amount of $SiCl_2$ to a cold zone without disproportionation; at lower temperatures it has reacted with $SiCl_4$ to form Si_2Cl_6, Si_3Cl_8[72] etc. Another important feature of this method is the ease with which corrosive, unstable vapour species are handled successfully and in a useful way, viz. transport of Al by the monochloride[73].

Disadvantages of the transpiration method

(1) The number of moles vaporizing cannot be known unless the molecular weight of the vapour is known.

(2) The difficult situation in this technique is to follow individual species in a heterogeneous system where the products of the reaction are more than one gaseous species.

Thus the study of reaction involved in the overall process becomes difficult. But improvements in the arrangements leading to quantitative collection of the products, depositing the condensate on the cold finger, quenching methods and improved analytical techniques may help to solve the problem.

1.2.5. THERMODYNAMICS AS APPLIED TO EQUILIBRIUM REACTIONS BY TRANSPIRATION

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

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

$$P = nRT/V_T \qquad \ldots(22)$$

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

$$P = \Sigma\, nRT_r/Vr \qquad \ldots(23)$$

The pressure of the various components in the reaction (equation 18) can thus be calculated as follows

$$P_C = \frac{c}{a}\,\frac{n_A\, RT_r}{V_r} \qquad \underline{\text{OR}} \qquad \frac{c}{a}\,\frac{\Delta W\, RT_r}{M\, V_r} \qquad \ldots(24)$$

$$P_{B\text{ unreacted}} = \left(n_B - \frac{b}{a}\,n_A\right)\frac{RT_r}{V_r} \qquad \ldots(25)$$

$$\underline{\text{OR}} \qquad \left(n_B - \frac{b}{a}\,\frac{\Delta W}{M}\right)\frac{RT_r}{V_r} \qquad \ldots(26)$$

The equilibrium constant $K = P_C^c/P_B^b$ ...(26A)

The equilibrium constant

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

$$\Delta F = 0 \qquad \ldots(27)$$

i.e. 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 (18) the

$$\Delta F^o = -RT \ln K \qquad \ldots(28)$$

1.2.6. TREATMENT OF THE EQUILIBRIUM DATA

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

Second Law Method

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

$$d\left(\frac{\Delta F^{o}}{T}\right) = \frac{\Delta H^{o}}{T^{2}}\, dT = \Delta H^{o}\, d\,\frac{1}{T} \qquad \ldots(29)$$

Substituting equation 28 for F^{o} in equation 29, one obtains the Vant Hoff's equation

$$\frac{d\ \ln k}{dT} = \frac{\Delta H^{o}}{RT^{2}} \quad \underline{\text{OR}} \quad \frac{d(R\ \ln k)}{d\left(\frac{1}{T}\right)} = \frac{4.5758\ d\ \log k}{d\left(\frac{1}{T}\right)} = -\Delta H^{o} \qquad \ldots(30)$$

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

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

$$\left[\frac{\partial(\Delta H^o)}{\partial T}\right]_p = \Delta C_p^o \qquad \ldots(31)$$

Therefore, if the heat capacity equations are available for the reactants and products an improved procedure is possible[74,75]. The treatment includes the use of the following equations

$$\frac{\Delta F}{T} = -R \ln k = \frac{\Delta H^o}{T} - a\ln T - \frac{1}{2} bT - \frac{1}{2} cT^{-2} + I \qquad \ldots(32)$$

where I is constant

$$\frac{\Delta H^o}{T} + I = \Sigma = -R \ln k + \Delta a \ln T + \frac{1}{2} \Delta bT + \frac{1}{2} + \Delta cT^{-2} \qquad \ldots(33)$$

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 Σ against 1/T gives a straight line with a slope ΔH_I^o. From the value of H_I^o one can obtain ΔH_T^o at any temperature range for which the heat capacity equations are applicable.

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

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 $\left(\frac{F_T^o - H_{T\,ref}^o}{T}\right)$ 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 Margrave[76].

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

$$\frac{\Delta F^{o}}{T} = \Delta H_T^o - T\Delta S_T^o \qquad \ldots(34)$$

one obtains

$$\frac{F_T^o - H_T^o}{T} = -S_T^o \qquad \ldots(35)$$

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

$$\frac{F_T^o - H_{T\ ref}^o}{T} = - S_T^o + \frac{H_T^o - H_{T\ ref}^o}{T} \qquad ...(36)$$

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

$$\frac{F_T^o - H_{298}^o}{T} = \frac{F_T^o - H_o^o}{T} - \frac{H_{298}^o - H_o^o}{T} \qquad ...(37)$$

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

$$S_T^o = \int_{T_o}^{T_1} C_p \, d\ln T + \frac{\Delta HT_r}{T_1} + \int_{T_1}^{T_2} C_p \, d\ln T + \int_{T_1}^{T} C_p \, d\ln T \qquad ...(38)$$

and

$$\frac{H_T^o - H_{T\ ref}}{T} = \frac{1}{T}\left[\int_{T\ ref}^{T_1} C_p \, dT + \Delta HT_r + \int_{T_1}^{T_2} C_p dT + \int_{T_1}^{T} C_p dT\right] \qquad ...(39)$$

In the case of gaseous molecules it is possible to determine the value of 'fef' directly through the use of statistical thermodynamics and spectroscopic data[77].

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

$$\Delta fef = (fef)_{products} - (fef)_{reactants} \qquad ...(40)$$

After collection of the terms and consolidation one obtains

$$\Delta \text{fef} + \frac{\Delta F_T^o}{T} - \frac{\Delta H_{T\ \text{ref}}^o}{T} \qquad \ldots.(41)$$

$$\Delta H_{T\ \text{ref}}^o = T \left(\frac{\Delta F_T^o}{T} - \Delta \frac{F_T^o - H_{T\ \text{ref}}^o}{T} \right) \qquad \ldots(42)$$

Substituting the equation 28 in equation 42 the equation can be written as:

$$\Delta H_{T\ \text{ref}}^o = T\ (-R \ln k - \Delta\ \text{'fef'}) \qquad \ldots(43)$$

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 the 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 difficult to eliminate from equilibrium measurements. The temperature coefficient and the corresponding heat of reaction from the second law may be greatly in error whereas the third law heat does not change significantly.

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CHAPTER - II

VAPOUR PRESSURES OF MANGANESE CHLORIDE
AND
THE EQUILIBRIUM STUDY OF THE REACTIONS

$$Mn(c) + MnCl_2(g) \rightleftharpoons 2MnCl(g)$$

AND

$$2Mn(c) + AlCl_3(g) = MnCl(g) + MnCl_2(g) + Al(l)$$

In view of these discrepancies, the equilibrium study of the reaction of $MnCl_2(g)$ with $Mn(c)$ at high temperatures has been undertaken, employing the transpiration technique.

Before carrying out the equilibrium study of the reaction

$$Mn(c) + MnCl_2(g) \rightleftharpoons 2MnCl(g) \qquad ...(1)$$

it is necessary to understand the vaporization behaviour of manganese dichloride.

SECTION - 1

VAPORIZATION OF MANGANESE DICHLORIDE

2.1.1. INTRODUCTION

The vapour pressures of manganese dichloride have been studied by static, transpiration as well as mass spectrometric methods. Maier[91] was the first to study the vaporization behaviour of a number of metal dichlorides by the static method using nitrogen as the buffer gas. Later Schäfer **et.al.**[92] carried out investigations on the vaporization phenomenon of the dichlorides of manganese, cobalt, iron, chromium and nickel, using transpiration method. They have shown that different carrier gases viz. N_2, A, HCl, have little or no effect on the vapour pressures except when chlorine is used at temperatures more than 800°C. Above 800°C in the case of chlorine as a carrier gas, the saturation pressures were different from those observed at temperatures below 800°C[93]. This is attributed to the formation of trichlorides.

The vaporization of a number of transition metal(II) halides has been studied by Schoonmaker **et.al.**[94] employing the mass spectrometer. They have attributed the irregularities in the vapour pressures of certain chlorides to the existence of the corresponding dimer according to

$$2MX_2(g) \; = \; M_2X_4(g) \qquad \ldots(44)$$

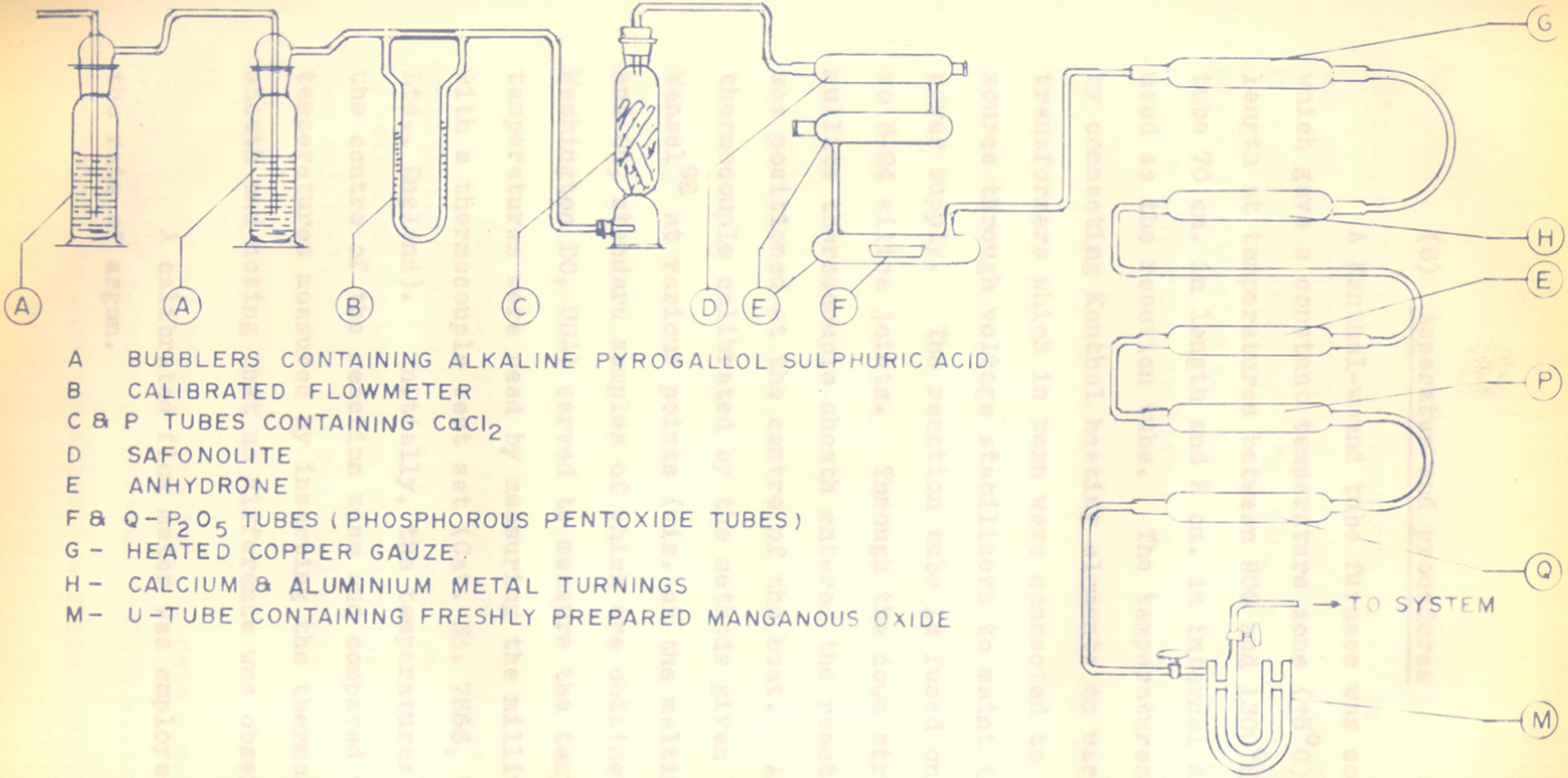
No such dimer is observed by them in the case of manganese chloride and hence it has been assumed in this study that $MnCl_2(g)$ vaporizes predominantly as a monomer.

2.1.2. EXPERIMENTAL

(A) Materials

(1) Manganese(II) chloride - Reagent grade manganese chloride tetrahydrate supplied by BDH was dehydrated in a stream of dry HCl gas followed by nitrogen at 220°C for about 2 hours[95]. The dichloride crystals were chemically analysed by standard methods of analysis[96] and found to be 99% pure.

(2) Argon - It is necessary to purify the argon gas as impurities like oxygen, moisture and nitrogen will react with manganese forming various oxides and nitrides. The gas was allowed to pass through a purification train schematically shown in Fig. 1. The train consisted of two bubblers containing alkaline pyrogallol and sulphuric acid respectively, a calibrated flow meter to regulate the gas and two columns containing $CaCl_2$ and P_2O_5 to remove moisture. Finally the gas was allowed to pass through a tube containing freshly reduced copper kept at 600°C and boats containing calcium turnings, aluminium metal and titanium sponge at about 700°C to remove traces of O_2 and N_2. Besides, freshly prepared manganous oxide[97] was used to remove oxygen up to less than 1 ppm.



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

FIG. I. PURIFICATION TRAIN FOR ARGON GAS.

(B) Apparatus and procedures

A Kanthal-wound tube furnace was constructed which gave a constant temperature zone (±5°C) of 15 cm. length at temperatures between 900 and 1300°K. A silica tube 70 cm. in length and 2 cm. in internal diameter was used as the reaction tube. The temperatures were obtained 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 reaction tube is fused on either side to B-24 silica joints. Through the down stream and a mullite thermocouple sheath entered the reaction tube and was positioned at the centre of the boat. A chromel-alumel thermocouple calibrated by the methods given by Roeser and Wensel[98] at various points (viz. at the melting points of Al and Cu, standard samples of which are obtained from N.B.S., Washington DC, USA) served to measure the temperature. The temperatures were read by measuring the millivolts at intervals with a thermocouple test set (Cat. No. 7556, W.G.Pye and Co. Ltd., England). Initially, the temperatures were measured in the centre of the reaction zone and compared with the temperatures measured by inserting the thermocouple in the sheath and noting that no difference was observed.

A calibrated flow meter was employed to measure the rate of argon.

In order to know the pressure in the system, the outcoming gas flow was connected to a U tube mercury manometer and the difference in the levels of mercury column was noted in a few experiments. The total pressure at which the system was in equilibrium was taken as the sum of barometric pressure and the difference in levels of the mercury in the manometer.

The reaction tube was completely flushed with purified argon gas. After attaining the required constant temperature and adjusting the argon gas rate to a desired value, the boat containing anhydrous manganese chloride was introduced from the downstream end and the experiment was started. Precautions were taken to avoid contaminating the carrier gas with air, while inserting and removing the boat in and out of the flow system. After running the experiment for a definite time (1 hour) the heating was stopped and the boat was pushed out of the zone. The boat and the substance were allowed to cool in the argon atmosphere.

In each run the amount of manganese chloride transported was found out by weight loss measurements. Loss in weight of the manganese chloride was also checked by chemical analysis of the residual manganese chloride.

2.1.3. EFFECT OF FLOW RATE

It had become necessary to determine the limits of flow rates of carrier gas where complete saturation occurred. This helped to know the extent to which the experimental results were being influenced by diffusion transport and also whether the equilibrium between a gas phase and a condensed phase was established or not. Keeping the temperature constant at 1148°K, the amount transported was studied by varying the flow rate of the carrier gas (containing $MnCl_2$) between 20 and 70 cc/min. The results are given in Table II. When the data for weight loss were plotted against the flow rates in the above range (Fig. 2) it increased linearly, thereby indicating that the flow gas was saturated with the gaseous products. The vaporization studies were carried out at different temperatures and the results are recorded in Table III.

2.1.4. TREATMENT OF THE DATA

In the study of vaporization of $MnCl_2$ over the temperature range 990-1220°K, the experimental weight loss data of $MnCl_2$ was used to calculate its vapour pressure which can be calculated from the equation

$$P = n\ RT_r/V_r \qquad \ldots(23)$$

where P = the pressure.

n = number of moles of $MnCl_2$ transported.

R = gas constant.

V_r = volume of the argon in litres at temperatures T_r°K.

TABLE - II

TRANSPORT OF $MnCl_2$ WITH CHANGE IN FLOW RATE OF ARGON AT 875°C

Expt. No.	Rate of flow of argon gas litres/hour	Wt. of $MnCl_2$ taken g.	$MnCl_2$ transported g.
1	0.80	0.3067	0.0467
2	0.91	0.3231	0.0661
3	1.20	0.3809	0.1307
4	1.76	0.3536	0.2194
5	2.28	0.5071	0.2708
6	3.01	0.5838	0.3793
7	3.89	0.6420	0.4759
8	4.50	0.7509	0.5306
9	5.03	0.8203	0.6514
10	5.19	0.9534	0.7055

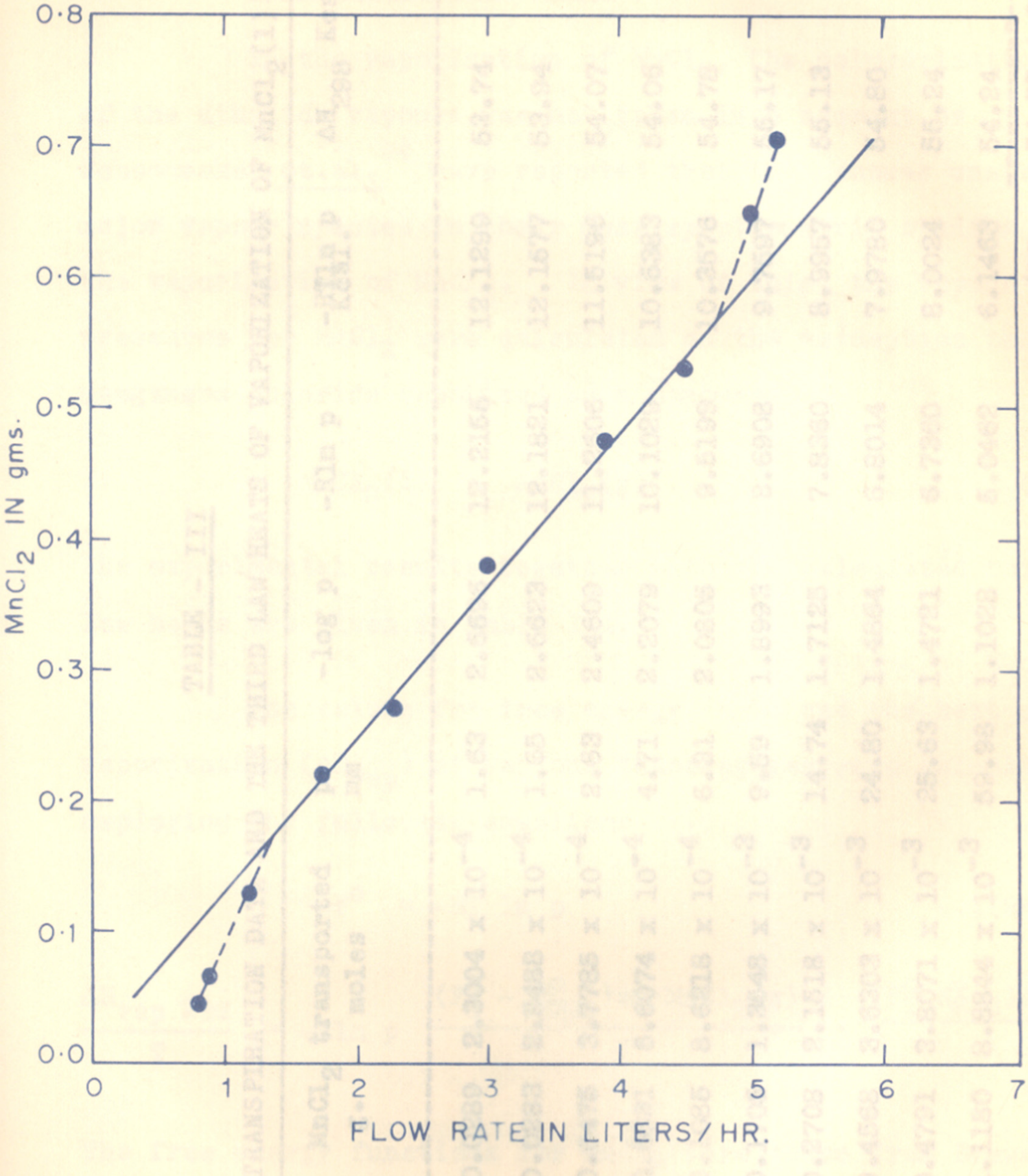


FIG. 2. PLOT OF TRANSPORT OF $MnCl_2$ VS FLOW RATE (ARGON).

TABLE - III

TRANSPIRATION DATA AND THE THIRD LAW HEATS OF VAPORIZATION OF $MnCl_2(l) \longrightarrow MnCl_2(g)$

Temp. ^oK	Rate of flow of argon gas lit./hr.	$MnCl_2$ g.	transported moles	p mm	-log p	-Rln p	-RTln p Kcal.	ΔH_{298} Kcal.
993	2.25	0.0289	2.3004×10^{-4}	1.63	2.6696	12.2155	12.1299	53.74
998	2.16	0.0283	2.2488×10^{-4}	1.65	2.6623	12.1821	12.1577	53.94
1023	2.28	0.0475	3.7785×10^{-4}	2.63	2.4609	11.2606	11.5196	54.07
1053	2.22	0.0831	6.6074×10^{-4}	4.71	2.2079	10.1029	10.6383	54.06
1088	2.22	0.1085	8.6218×10^{-4}	6.31	2.0805	9.5199	10.3576	54.78
1123	2.22	0.1705	1.3548×10^{-3}	9.59	1.8993	8.6908	9.7597	55.17
1148	2.28	0.2708	2.1518×10^{-3}	14.74	1.7125	7.8360	8.9957	55.13
1173	2.25	0.4568	3.6303×10^{-3}	24.80	1.4864	6.8014	7.9780	54.80
1188	2.28	0.4791	3.8071×10^{-3}	25.63	1.4721	6.7360	8.0024	55.24
1218	2.16	1.1180	8.8844×10^{-3}	59.98	1.1028	5.0462	6.1463	54.24
							Avr.	54.52 ± 0.78

2.1.5. RESULTS AND DISCUSSION

In the vaporization of $MnCl_2$, the polymerization of the dihalide vapours was not taken into account as Schoonmaker et.al.[94] have reported that the monomer was the major vapour species in their mass spectrometric studies on the vaporization of $MnCl_2$. In view of this, the vapour pressures for $MnCl_2$ were calculated on the assumption that manganese chloride vaporized as a monomer

$$MnCl_2(l) = MnCl_2(g) \qquad \ldots(45)$$

The experimental results together with the calculated third law heats are given in Table III.

The values for free energy (ΔF^o) and the heat of vaporization (ΔH_{vap}) at various temperatures were calculated employing the following equations

$$\Delta F^o = -RT \ln p \qquad \ldots(28)$$

$$\frac{\Delta H_{vap\ 298}}{T} = -R\ln p \quad \frac{(F_T^o - H_{298}^o) \text{of } MnCl_2(g)}{T} - \frac{(F_T^o - H_{298}^o) \text{of } MnCl_2(l)}{T} \qquad \ldots(46)$$

The free energy functions for $MnCl_2$ were taken from Brewer and Somayajulu[99] and Kelley[100,101].

The vapour pressure equation can be given by:

$$\text{Log } P_{atm} = \frac{-7.729 \pm 277.48}{T} + 5.1079 \pm 0.25 \qquad ...(47)$$

Employing the Vant Hoff's equation

$$d \ln P/d(1/T) = -\frac{\Delta H_{vap}}{R} \qquad ...(48)$$

the heat of vaporization ΔH_v was determined from the plot of the logarithm of the equilibrium constant versus the reciprocal of the absolute temperature (Fig. 3). The slope of the line obtained by the method lf least squares gave the second law heat $\Delta H_{1106} = 35.37 \pm 1.27$ Kcal. This represented the mean value over the temperature range studied and did not take into account the effect of the C_p. According to Brewer[102] the change in the C_p is -10 cal. deg.$^{-1}$ mole^{-1}, when a bivalent halide changes from a solid to gas. This difference in the C_p values when integrated between the limits 298 and 1106 gives $\Delta(H^o_{1106} - H^o_{298})$

$$\int_{298}^{1106} C_p dT = \Delta(H^o_{1106} - H^o_{298}) \qquad ...(49)$$

$$\Delta C_p = (1106 - 298) = \Delta(H^o_{1106} - H^o_{298}) \qquad ...(50)$$

$$-10\ (1106-298) = 8.08 \text{ Kcal.} \qquad ...(51)$$

This when added to the above value of heat of vaporization at 1106°K yields 43.45 ± 1.27 Kcal. Using the heat of

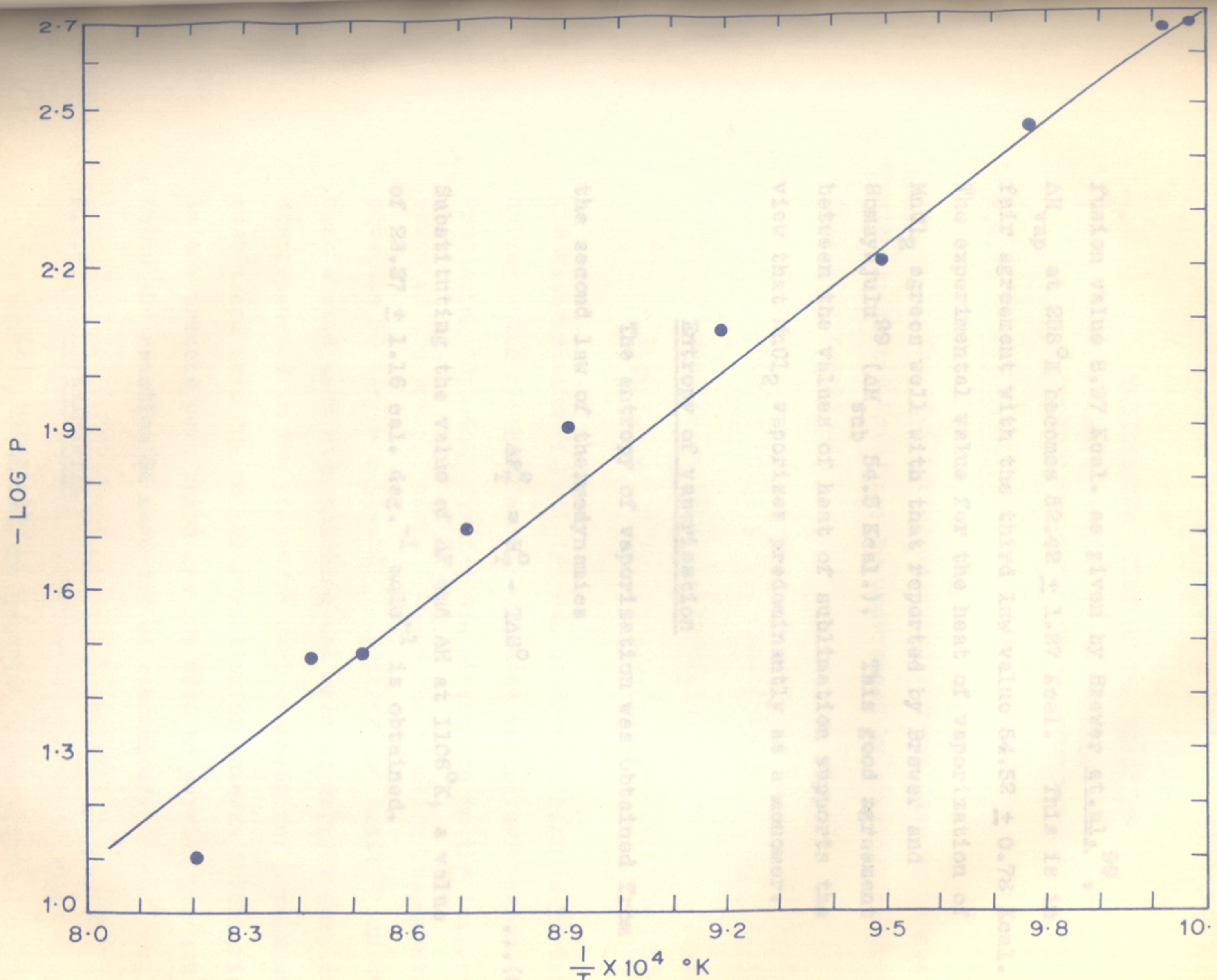


FIG. 3. PLOT OF LOG P VS $^1/_T$ FOR THE VAPORIZATION OF $MnCl_2(l) = MnCl_2(g)$

fusion value 8.97 Kcal. as given by Brewer et.al.[99], ΔH_{vap} at 298°K becomes 52.42 ± 1.27 Kcal. This is in fair agreement with the third law value 54.52 ± 0.78 Kcal. The experimental value for the heat of vaporization of $MnCl_2$ agrees well with that reported by Brewer and Somayajulu[99] (ΔH_{sub} 54.5 Kcal.). This good agreement between the values of heat of sublimation supports the view that $MnCl_2$ vaporizes predominantly as a monomer.

Entropy of vaporization

The entropy of vaporization was obtained from the second law of thermodynamics

$$\Delta F_T^o = H_T^o - T\Delta S^o \qquad \ldots(52)$$

Substituting the value of ΔF and ΔH at 1106°K, a value of 23.37 ± 1.16 cal. $deg.^{-1}$ $mole^{-1}$ is obtained.

SECTION - 2

EQUILIBRIUM STUDY OF THE REACTION $Mn(c) + MnCl_2(g) \rightleftharpoons 2MnCl(g)$

2.2.1. INTRODUCTION

The equilibrium reaction between gaseous manganese dichloride and Mn(c) may be understood by considering the following reactions

$$Mn(c) + MnCl_2(g) \rightleftharpoons 2MnCl(g) \qquad ...(1)$$

$$MnCl_2(g) = MnCl(g) + 1/2\ Cl_2(g) \qquad ...(53)$$

$$MnCl_2(g) + 1/2\ Cl_2(g) = MnCl_3(g) \qquad ...(54)$$

The vaporization of $MnCl_2(g)$ was studied at high temperatures during which no chlorine was observed in the exit gases indicating that $MnCl_2(g)$ did not dissociate in the temperature range of the present work. Hence the reaction represented by equation 53 can be neglected. Schäfer and Breil[93] in their work stated that when chlorine was used as carrier gas, small discrepancies in the pressures were observed and concluded that these were due to the formation of gaseous trichloride. In the present work argon gas was used as carrier gas and hence the reaction 54 need not be considered.

2.2.2. EXPERIMENTAL

(A) Materials

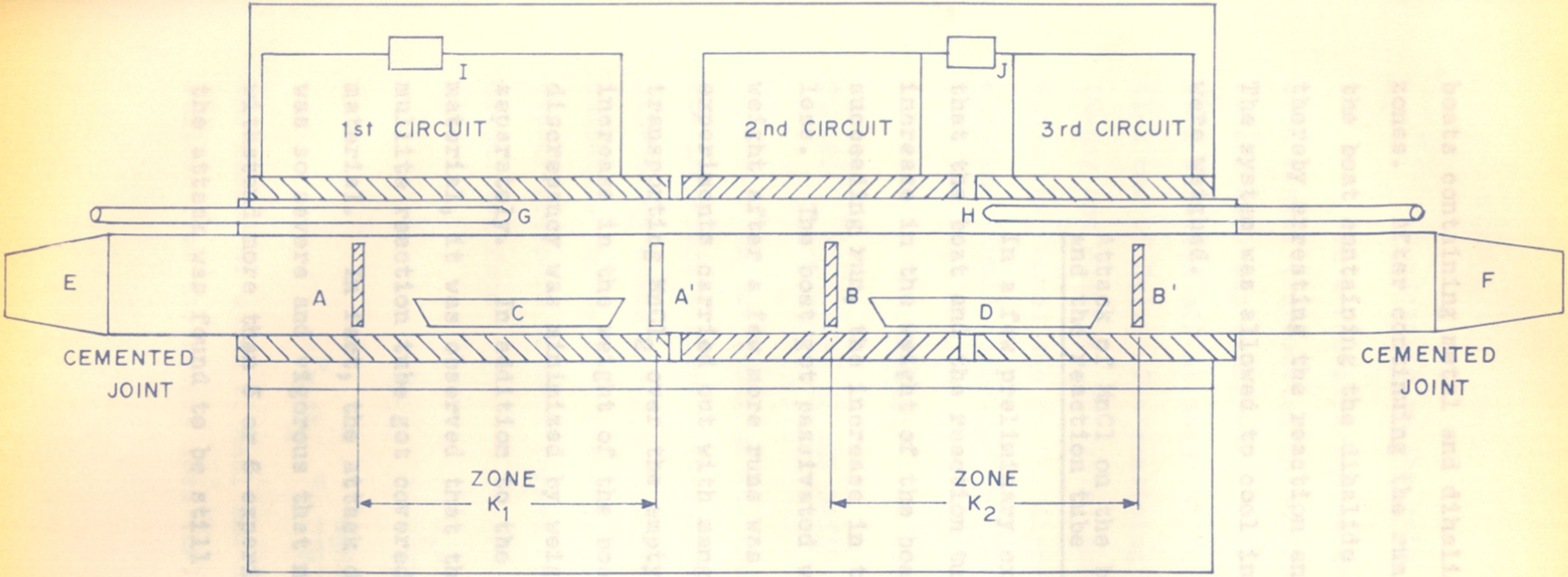
(1) Manganese metal flakes of 99.995 per cent purity supplied by Koch-Light Laboratories Ltd., England, were used.

(2) Manganese(II) chloride - Purified and anhydrous (described earlier) $MnCl_2$ was used.

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

(B) Apparatus and procedure

To study this reaction a special tube furnace (Fig.4) wound with Kanthal-A heating element was constructed, which could give two different constant temperature zones K_1 and K_2, each nearly 10 cm. in length and with a temperature variation of $\pm 8^\circ C$. This was necessary to prevent the condensation of manganese chloride vapour in the middle of the reaction tube. The constant temperature zones were long enough to accommodate two boats (C and D). The insulation around the heating elements consisted of light refractory bricks commercially called "Bagsvic". A mullite refractory tube (length 100 cm., internal diameter 1.5 cm.) was used as the reaction tube. B-24 Pyrex joints were connected to either end of the tube with a high alumina refractory cement (Accoset-50 supplied by M/s. Associated Cement Company Ltd., India) which helped to give cemented gas tight joints. The boat C containing manganese chloride was kept at about $1150^\circ K$. After attaining the constant temperature in the reaction zone, the boat containing manganese metal was introduced in the tube from the downstream end. The argon rate was regulated to the desired value and the experiment was started by pushing



A, B
A', B' RADIATION SHIELDS

C, D – BOATS CONTAINING METAL HALIDE AND METAL

E, F – B_{24} MALE GLASS JOINTS

G, H – THERMOCOUPLE SHEATHS

I, J – VARIACS CONNECTED THROUGH VOLTAGE STABILIZER

K_1, K_2 – CONSTANT TEMPERATURE ZONES

FIG. 4. FURNACE FOR THE STUDY OF THE EQUILIBRIUM REACTION $Mn_{(c)} + MnCl_{2(g)} = 2MnCl_{(g)}$

boats containing metal and dihalide in their respective hot zones. After continuing the run for definite period (1 hour) the boat containing the dihalide was pushed out of the hot zone thereby arresting the reaction and the heating was stopped. The system was allowed to cool in argon and both the boats were weighed.

Attack of MnCl on the boat and the reaction tube

In a few preliminary experiments it was observed that the boat and the reaction tube were attacked and an increase in the weight of the boat was noticed. After each succeeding run, the increase in the weight was found to be less. The boat got passivated when the increase in its weight after a few more runs was negligible. Blank experiments carried out with manganese metal and by transporting $MnCl_2$ over the empty boat showed no perceptible increase in the weight of the boat. The experimental discrepancy was minimized by weighing the metal flakes separately. In addition to the attack of MnCl on the boat material, it was observed that the inner surface of the mullite reaction tube got covered with a thin layer of black material. In fact, the attack due to highly corrosive MnCl was so severe and vigorous that no mullite reaction tube could withstand more than 5 or 6 experiments. At higher temperatures the attack was found to be still more severe.

Condensate on the cold finger

In a few experiments the condensate on the silica cold finger (introduced in the reaction tube from the downstream end) was examined. Pink deposit of $MnCl_2$ crystals was ~~were~~ sublimed off at about 800°C under reduced pressure (1-2 mm. of Hg). The remaining black deposit on analysis (X-ray and chemical analysis) showed the presence of Mn-metal which was formed due to the disproportionation of the monochloride (MnCl) according to the following equation

$$2MnCl(g) \longrightarrow 2Mn(c) + MnCl_2(g) \qquad \ldots(55)$$

2.2.3. TREATMENT OF THE DATA

In the study of the equilibrium reaction 1 over the temperature range 1240-1410°K, the experimentally determined weight loss data of Mn and $MnCl_2$ were used to calculate the partial pressures of MnCl and $MnCl_2$. The vapour pressure of MnCl formed during the reaction was calculated from

$$P_{MnCl} = \frac{n_a RT_r}{V_r} \qquad \ldots(56)$$

$$P_{MnCl_2} = \frac{n_b RT_r}{V_r} \qquad \ldots(57)$$

The number of moles of MnCl and $MnCl_2$ were calculated as follows from the weight loss (ΔW) data of Mn and $MnCl_2$

$$n_a = \frac{2 \times \Delta W \text{ Mn}}{\text{mol.wt.Mn}} \qquad \ldots(58)$$

$$n_b = \frac{\Delta W \text{ MnCl}_2}{\text{mol.wt.MnCl}_2} \qquad \ldots(59)$$

The equilibrium constant K_p can be calculated from the equation

$$K_p = p^2a/P_b \qquad \ldots(60)$$

2.2.4. RESULTS AND DISCUSSION

The experimental results and the transpiration data are presented in Table IV. The free energies and the heats of reaction at various temperatures were calculated employing the equation 28. The free energy functions for products and reactants are taken from Kelley[100,101] and Brewer and Somayajulu[99]. The free energies and the calculated third law heats for the reaction 1 have been summarised in Table V.

Employing the Vant Hoff's equation, the heat of reaction ΔH_r has been determined from the plot of log K vs. 1/T (Fig.5). The slope of the line obtained by the method of least squares gave the heat of reaction $\Delta H_r = 47.34 \pm 1.64$ Kcal. This value of ΔH_r represents the mean over the temperature range studied and did not include the C_p values. The value for $\Delta H_{r\ 298}$ could be calculated from the knowledge of

TABLE IV

TRANSPIRATION DATA FOR THE EQUILIBRIUM REACTION $Mn(c) + MnCl_2(g) \rightleftharpoons 2MnCl(g)$

Temp. ^oK	Rate of flow of argon gas lit./hr.	$MnCl_2$ passed g.	Loss in Mn metal mg.	P_{MnCl} atm.	P_{MnCl_2} atm x 10^{-2}	K_p	-log K_p
1243	2.16	0.3999	9.10	3.7877×10^{-3}	3.4439	4.1657×10^{-4}	3.3803
1273	2.16	1.1033	22.22	9.2486×10^{-3}	9.5618	8.9456×10^{-4}	3.0484
1293	2.22	0.7108	19.20	7.7756×10^{-3}	5.8948	1.0256×10^{-3}	2.9890
1333	2.25	0.8540	25.25	1.0089×10^{-2}	6.9444	1.4658×10^{-3}	2.8339
1363	2.22	0.5034	23.40	9.4765×10^{-3}	3.9782	2.2574×10^{-3}	2.6464
1373	2.40	1.1050	40.95	1.5340×10^{-2}	8.2687	2.8458×10^{-3}	2.5458
1388	2.58	1.1282	46.85	1.6326×10^{-2}	7.7656	3.4323×10^{-3}	2.4644
1413	2.40	0.8402	46.95	1.7587×10^{-2}	5.9911	5.1631×10^{-3}	2.2871

TABLE - V

FREE ENERGY AND THIRD LAW HEATS FOR THE REACTION $Mn(c) + MnCl_2(g) \rightleftharpoons 2MnCl(g)$

Temp. °K	$-\log K_p$	$-R\ln K_p$	$-RT\ln K_p$ Kcal.	$-\Delta\left(\frac{F_T - H_{298}}{T}\right)$	$\Delta H_{r\,298}$ Kcal.	$\Delta H_{f\,298}^{MnCl}$ Kcal.
1243	3.3803	15.4676	19.2262	37.46	65.79	2.54
1273	3.0484	13.9489	17.7568	37.32	65.27	2.28
1293	2.9890	13.6771	17.6845	37.23	65.82	2.56
1333	2.8339	12.9673	17.2854	37.08	66.71	3.00
1363	2.6464	12.1094	16.5051	36.96	66.89	3.09
1373	2.5458	11.6491	15.9942	36.93	66.70	3.00
1388	2.4644	11.2766	15.6519	36.87	66.83	3.06
1413	2.2871	10.4653	14.7875	36.78	66.76	3.03
					Avr. 66.35 ± 1.1	Avr 2.82 ± 0.54

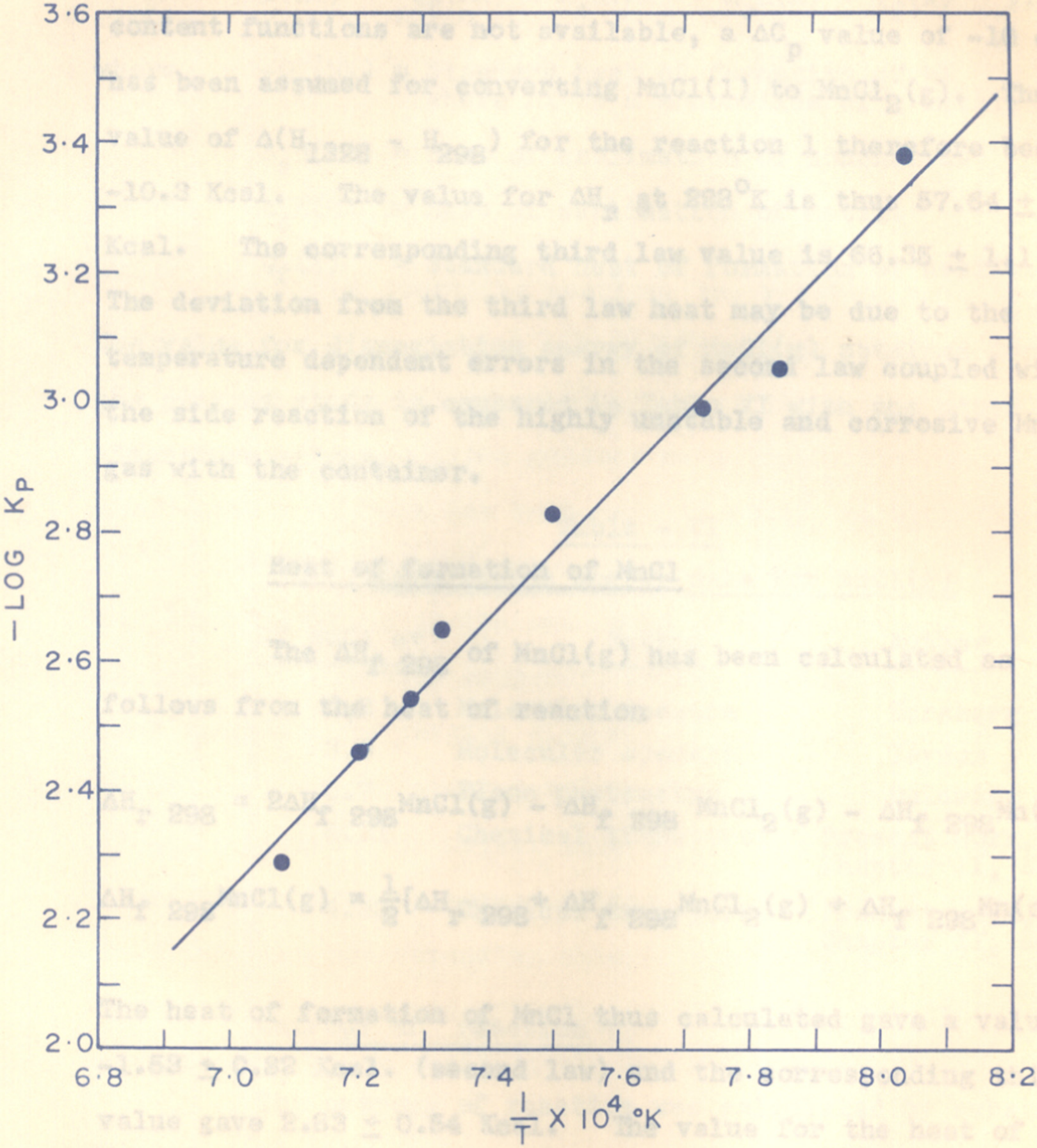


FIG. 5. PLOT OF LOG K_P VS $1/T \times 10^4$ OF THE REACTION $Mn(c) + MnCl_2(g) \rightleftharpoons 2MnCl(g)$

ΔH_{1328} and the functions cited by Kelley[100]. As the heat content functions are not available, a ΔC_p value of -10 cal.[102] has been assumed for converting MnCl(1) to $MnCl_2(g)$. The value of $\Delta(H_{1328} - H_{298})$ for the reaction 1 therefore becomes -10.3 Kcal. The value for ΔH_r at 298°K is thus 57.64 ± 1.64 Kcal. The corresponding third law value is 66.35 ± 1.1 Kcal. The deviation from the third law heat may be due to the temperature dependent errors in the second law coupled with the side reaction of the highly unstable and corrosive MnCl gas with the container.

Heat of formation of MnCl

The $\Delta H_{f\ 298}$ of MnCl(g) has been calculated as follows from the heat of reaction

$$\Delta H_{r\ 298} = 2\Delta H_{f\ 298}MnCl(g) - \Delta H_{f\ 298}\ MnCl_2(g) - \Delta H_{f\ 298}Mn(c) \quad ..(61$$

$$\Delta H_{f\ 298}MnCl(g) = \frac{1}{2}\left[\Delta H_{r\ 298} + \Delta H_{f\ 298}MnCl_2(g) + \Delta H_{f\ 298}Mn(c)\right] \quad ...(62$$

The heat of formation of MnCl thus calculated gave a value of -1.53 ± 0.82 Kcal. (second law) and the corresponding third law value gave 2.83 ± 0.54 Kcal. The value for the heat of formation of $MnCl_2(g)$ (-60.7) was taken from Brewer and Somayajulu[99].

Dissociation energy of MnCl

The D_0^o for MnCl was calculated from ΔH_{f298} of MnCl(g) employing the following equation[103]

$$D(MX) = -Q_f(MX) - \Delta_s H(MX) + \Delta_s H(M) + Q_f(X) \quad \ldots(63)$$

where

$-Q_f(MX)$ = Standard heat of formation of MX where MX is a monohalide of a metal.

$\Delta_s H(MX)$ = Heat of sublimation of monohalide.

$\Delta_s H(M)$ = Heat of sublimation of metal.

$Q_f(X)$ = Standard heat of formation of halide.

The value for dissociation energy of MnCl(g) obtained from the present study is compared in Table VI with the other literature values.

Table - VI

Dissociation energy data for MnCl(g)

D_0^o MnCl ev	Method	Author
3.3	Molecular spectra	Herzberg
3.0	Molecular spectra	Gaydon
3.7	Flame photometry	Bulewicz
4.21	Chemical transport	Present work, Chapter II, Sec.2.
4.32	Chemical transport	Present work, Chapter II, Sec.3.

Entropy of reaction

The entropy of reaction was calculated by substituting the values for ΔF_{1328} and ΔH_{1328} in the equation 52. Thus a value of 22.83 ± 1.24 cal. deg.^{-1} mole^{-1} was obtained for the entropy of reaction at 1328°K.

SECTION - 3

STUDY OF THE REACTION

$2Mn(c) + AlCl_3(g) = MnCl_2(g) + MnCl(g) + Al(l)$

2.3.1. INTRODUCTION

In the preceding section, the reaction of a metal with its anhydrous gaseous chloride has been studied. It was thought worthwhile to study the reactions of a metal with dissimilar anhydrous gaseous metal chlorides and therefore an attempt has been made to study the reaction of manganese metal with aluminium trichloride. Lee[78] in his investigations on the transport of metals by gaseous chlorides at elevated temperatures has studied a number of such reactions by passing dissimilar anhydrous gaseous chlorides over different metals and alloys. When gaseous $AlCl_3$ is passed over metals like Ga, Fe and Ti, the products found by him are the corresponding alloys of Ga-Al, Fe-Al and Ti-Al and the corresponding chlorides of both the metals. Similarly when vapours of $GaCl_2$, $GeCl_4$, $SiCl_4$ and $TiCl_4$ were passed over Al, he obtained alloys of Ga-Al, Ge-Al, Si-Al and Ti-Al.

In the reaction of Mn(c) + $AlCl_3(g)$, the analysis of the products showed the presence of aluminium metal in the boat. However, the formation of traces of Mn-Al alloy are not ruled out. In the Al-Mn phase diagram[104,105] at the

Mn-rich end, the relevant curve given is the solubility of Al in alpha manganese. The solubility curves of Al in both α-Mn and β-Mn (in the Mn-rich region) are nearly parallel to the T-axis and hence only negligible heat effects (1 to 3 Kcal./gm. atom of Al) are probably involved. In order to establish the reaction scheme, equilibrium measurements were carried out at different temperatures together with the identification of the products.

2.3.2. EXPERIMENTAL

(A) Materials

(1) Manganese metal - 99.99% pure manganese metal was used in the study.

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

(3) Argon - purified argon gas as described earlier was used as carrier gas.

(B) Apparatus and procedure

A platinum wound tube furnace 50 cm. in length with three circuits was constructed. The outer two circuits with equal resistances were used to minimize the heat losses.

The furnace gave a constant temperature zone (± 10°C) between 1000 and 1500°K which was long enough to accommodate a boat containing Mn metal. The reaction tube made of mullite refractory (supplied by M/s. Kumar Mfg. Co. Ltd., Calcutta) of 60 cm. length and 2 cm. i.d. was introduced in the furnace.

Sections of pyrex glass tubing of suitable sizes were connected to both ends of the reaction tube with high alumina refractory cement (Accoset 50) to give cemented gas tight joints. In the pyrex tube at the upstream end (45 cm. length and 2.5 cm. i.d.) a glass boat (1 x 1 x 8 cm.) containing anhydrous aluminium trichloride was introduced. The temperature of the glass section was maintained at 150 ± 2°C to facilitate uniform transport of the halide by argon gas. The $AlCl_3$ vaporization furnace was connected to a variable voltage transformer through a voltage stabilizer. The furnace had also a sliding arrangement to facilitate arresting the reaction quickly by pushing it out after the run. Temperatures were measured by calibrated chromel-alumel and Pt-Pt-10% Rh thermocouples. A calibrated flow meter was employed to measure the flow of argon. A silica sheath was introduced from the downstream end which acted as a cold finger to facilitate the study of condensates obtained from gaseous reaction products.

The experiments were carried out by allowing the carrier gas saturated with $AlCl_3$ vapour to react with Mn-metal under equilibrium conditions. The products in the boat after the experiment were weighed and analysed by the standard methods of chemical analysis.

The gaseous products of the reaction carried away by the argon gas were condensed on the cold finger. After the experimental run of one hour the heating of $AlCl_3$ was stopped and the system was cooled in the argon gas flow. The boat containing $AlCl_3$ was weighed to know the amount of $AlCl_3$ transported.

2.3.3. IDENTIFICATION OF THE PRODUCTS

The residue in the boat containing unreacted manganese metal and small particles of shining grey metal was finely ground. X-ray analysis of the sample revealed the presence of Mn and aluminium.

The outcoming gases were examined and found to be chlorides of Al and Mn. Further identification of gaseous products was carried out by condensing them on the cold finger. The cold finger with the condensate was initially heated at 150°C under reduced pressure (1 to 2 mm. of Hg) to drive off the $AlCl_3$ and then the temperature was raised to about 800° when all the manganese chloride sublimed off leaving behind a black mass. Chemical and X-ray analysis of the mass showed it to be manganese metal. It is possible that Mn metal was formed by the disproportionation of gaseous MnCl according to the equation

$$2MnCl(g) \longrightarrow Mn(c) + MnCl_2(g) \qquad ...(55)$$

2.3.4. ANALYSIS OF THE RESIDUE

The substance that remained in the boat after the experiment was treated with hydrochloric acid and the solution was made to a definite volume. An aliquot was taken for the determination of manganese gravimetrically by standard phosphate method. Aluminium was determined colorimetrically using aluminon reagent as the quantities were very small. The manganese obtained corresponds to the unreacted quantity and by deducting it from the initial weight of manganese, the reacted amount was calculated. From the quantity of aluminium metal found in the boat the stoichiometry of the chemical reaction has been decided.

2.3.5. TREATMENT OF THE DATA

The vapour pressures of $MnCl_2(g)$, $MnCl(g)$ and $AlCl_3(g)$ were calculated from the experimentally determined weight loss data of manganese in the reaction represented by equation 74. Assuming that the ideal gas law holds good in the equilibrium zone, the partial pressures of the various components were calculated as follows:

$$P_{MnCl_2} = 1/2 \times n\ Mn \times RT_r/V_r \qquad ...(64)$$

$$P_{MnCl} = 1/2 \times n\ Mn \times RT_r/V_r \qquad ...(65)$$

$$P_{AlCl_3} = (n\ AlCl_3 - 1/2\ n\ Mn)\ RT_r/V_r \qquad ...(66)$$

where P_{MnCl_2}, P_{MnCl} and P_{AlCl_3} denote the partial pressures of the respective components and V_r represents the volume of the flow gas passed at the room temperature T_r and R being the gas constant. n $AlCl_3$ and n Mn denote the number of moles of the respective components.

The equilibrium constant K_p was calculated from the above partial pressures

$$K_p = \frac{(P_{MnCl_2})(P_{MnCl})}{(P_{AlCl_3})} \qquad ...(67)$$

It may be stated that the dimer $Al_2Cl_6(g)$ is not an important species at these temperatures of study.

2.3.6. POSSIBLE EQUILIBRIUM REACTIONS

In order to understand the reaction scheme, the following stoichiometries were considered

$$3Mn(c) + 2AlCl_3(g) = MnCl_2(g) + 2MnCl(g) + 2AlCl(g) \qquad ...(68)$$

$$2Mn(c) + AlCl_3(g) = 2MnCl(g) + AlCl(g) \qquad ...(69)$$

$$3Mn(c) + AlCl_3(g) = 3MnCl(g) + Al(l) \qquad ...(70)$$

$$3Mn(c) + 2AlCl_3(g) = 3MnCl_2(g) + 2Al(l) \qquad ...(71)$$

$$Mn(c) + AlCl_3(g) = MnCl_2(g) + AlCl(g) \qquad ...(72)$$

$$Mn(c) + AlCl(g) = MnCl(g) + Al(l) \qquad ...(73)$$

$$2Mn(c) + AlCl_3(g) = MnCl_2(g) + MnCl(g) + Al(l) \qquad ...(74)$$

Reactions 68 and 69 could be rejected on the basis that AlCl was not one of the final products as no aluminium metal [disproportionation of AlCl(g) gives Al metal and $AlCl_3$(g)] was observed on the cold finger. Reactions 70 and 71 were rejected as the study has revealed both dichloride and monochloride to be the reaction products. Consequently the reaction 74 has been given consideration. Here it may be pointed out that the reaction 74 can be said to consist of the reaction 72 and 73.

The calculated free energies for possible reactions at different temperatures were tabulated in Table VII. The change in free energy with temperature is shown in Fig.6. From the data and the graph it is evident that reactions 72 and 73 are more favourable at these temperatures, supporting the view point that reaction 74 is more thermodynamically feasible. However, the reaction is quite complicated to study employing the transpiration technique.

2.3.7. RESULTS AND DISCUSSION

The free energies are calculated by the equation

$$\Delta F = -RT \ln K_p \qquad \ldots(28)$$

The transpiration data and calculated equilibrium constants are given in Table VIII. The free energy and the calculated

TABLE - VII

CALCULATED FREE ENERGIES FOR POSSIBLE REACTIONS AT DIFFERENT TEMPERATURES

Equation No.	Reaction	Temp °K 1000	1100	1200	1300	1400	1500
68	$3Mn(c) + 2AlCl_3(g) = MnCl_2(g) + 2MnCl(g) + 2AlCl(g)$	67.214	55.655	44.091	32.819	21.555	10.730
69	$2Mn(c) + AlCl_3(g) = 2MnCl(g) + AlCl(g)$	43.282	35.812	28.363	21.101	13.866	6.896
70	$3Mn(c) + AlCl_3(g) = 3MnCl(g) + Al(l)$	50.398	42.326	34.244	26.422	18.608	11.188
71	$3Mn(c) + 2AlCl_3(g) = 3MnCl_2(g) + 2Al(l)$	42.746	36.747	30.585	24.696	18.683	13.189
72	$Mn(c) + AlCl_3(g) = MnCl_2(g) + AlCl(g)$	23.870	19.843	15.730	11.720	7.688	3.834
73	$Mn(c) + AlCl(g) = MnCl(g) + Al(l)$	7.120	6.520	5.880	5.320	4.740	4.290
74	$2Mn(c) + AlCl_3(g) = MnCl_2(g) + MnCl(g) + Al(l)$	31.048	26.358	21.610	17.039	12.431	8.126

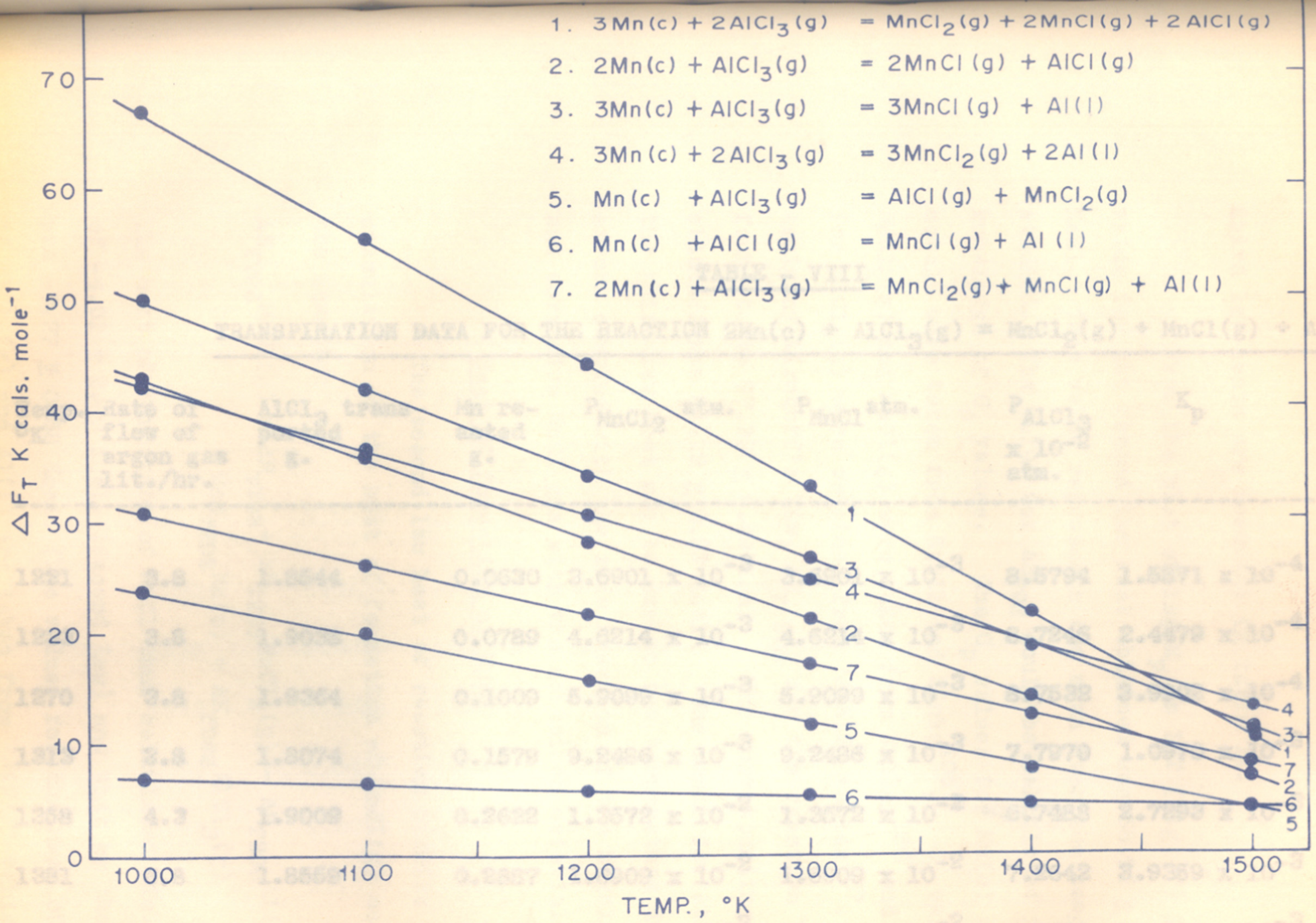


FIG. 6. CHANGE OF ΔF_T VS TEMPERATURE FOR VARIOUS REACTIONS.

TABLE - VIII

TRANSPIRATION DATA FOR THE REACTION $2Mn(c) + AlCl_3(g) = MnCl_2(g) + MnCl(g) + Al(l)$

Temp. °K	Rate of flow of argon gas lit./hr.	$AlCl_3$ transported g.	Mn reacted g.	P_{MnCl_2} atm.	P_{MnCl} atm.	P_{AlCl_3} x 10^{-2} atm.	K_p	-log K_p
1221	3.8	1.8544	0.0630	3.6901×10^{-3}	3.6901×10^{-3}	8.5794	1.5871×10^{-4}	3.7993
1233	3.8	1.9038	0.0789	4.6214×10^{-3}	4.6214×10^{-3}	8.7246	2.4479×10^{-4}	3.6112
1270	3.8	1.9364	0.1009	5.9099×10^{-3}	5.9099×10^{-3}	8.7532	3.9902×10^{-4}	3.3990
1313	3.8	1.8074	0.1579	9.2486×10^{-3}	9.2486×10^{-3}	7.7970	1.0970×10^{-3}	2.9601
1358	4.3	1.9009	0.2622	1.3572×10^{-2}	1.3572×10^{-2}	6.7488	2.7293×10^{-3}	2.5640
1381	3.8	1.8559	0.2887	1.6909×10^{-2}	1.6909×10^{-2}	7.2642	3.9359×10^{-3}	2.4049
1403	3.6	1.6948	0.3509	2.1695×10^{-2}	2.1695×10^{-2}	6.4628	7.2828×10^{-3}	2.1377

Each experiment was carried out for 1 hour.

third law heats are recorded in Table IX.

From the plot of log K_p vs 1/T (Fig. 7) the value for the second law heat obtained was 68.93 ± 2.49 Kcal. This value represents the mean over the temperature studied. The value for ΔH_{298} could be calculated from the knowledge of C_p values. The C_p values for Mn(c) and Al(l) metals were taken from Stull and Sinke[106], C_p values for $MnCl_2(g)$ and MnCl(g) were taken from Kelley[100] and C_p values for $AlCl_3(g)$ were obtained from 'JANAF' tables[107]. By applying Kirchoff's Law, $\Delta H_{r\ 298}$ for the reaction 74 was found to be 77.39 ± 2.49 Kcal. The corresponding third law obtained was 81.12 ± 0.93 Kcal. The small deviation from the third law heat may be due to the temperature dependant errors coupled with the side reaction of the highly unstable and corrosive MnCl gas with the container material.

Heat of formation of MnCl

The second law heat of reaction permits the calculation of the heat of formation of MnCl(g) according to the equation

$$\Delta H_{f298}MnCl(g) = \Delta H_{r298} - \Delta H_{f298}MnCl_2(g) - \Delta H_{f298}Al(l) + 2\Delta H_{f298}Mn(c) + \Delta H_{f298}AlCl_3(g) \qquad \ldots(75)$$

The heat of formation of MnCl thus calculated yielded a value of -4.01 ± 2.49 Kcal. (Second Law) and that by the third law was -0.27 ± 0.68 Kcal. (The values for the heat of formation of $AlCl_3(g)$ and Al(l) are taken from 'JANAF' tables[107]).

TABLE - IX

FREE ENERGY AND THE THIRD LAW HEATS FOR THE REACTION $2Mn(c) + AlCl_3(g) = MnCl_2(g) + MnCl(g) + Al(l)$

Temp. °K	$-\log K_p$	$-R\ln K_p$	$-RT\ln K_p$ Kcal.	$-\Delta\left(\frac{F_t - H_{298}}{T}\right)$	ΔH_{r298} Kcal.	ΔH_{f298}^{MnCl} Kcal.
1221	3.7993	17.3848	21.2268	48.535	80.49	-0.91
1233	3.6112	16.5241	20.3742	48.510	80.19	-1.21
1270	3.3990	15.5531	19.7524	48.425	81.25	-0.15
1313	2.9601	13.5448	17.7843	48.365	81.29	-0.11
1358	2.5640	11.7323	15.9325	48.270	81.48	+0.08
1381	2.4049	11.0043	15.1969	48.235	81.81	+0.41
1403	2.1377	9.7817	13.7237	48.215	81.37	-0.03
					Avr. 81.12 ± 0.93	Avr. -0.27 ± 0.68

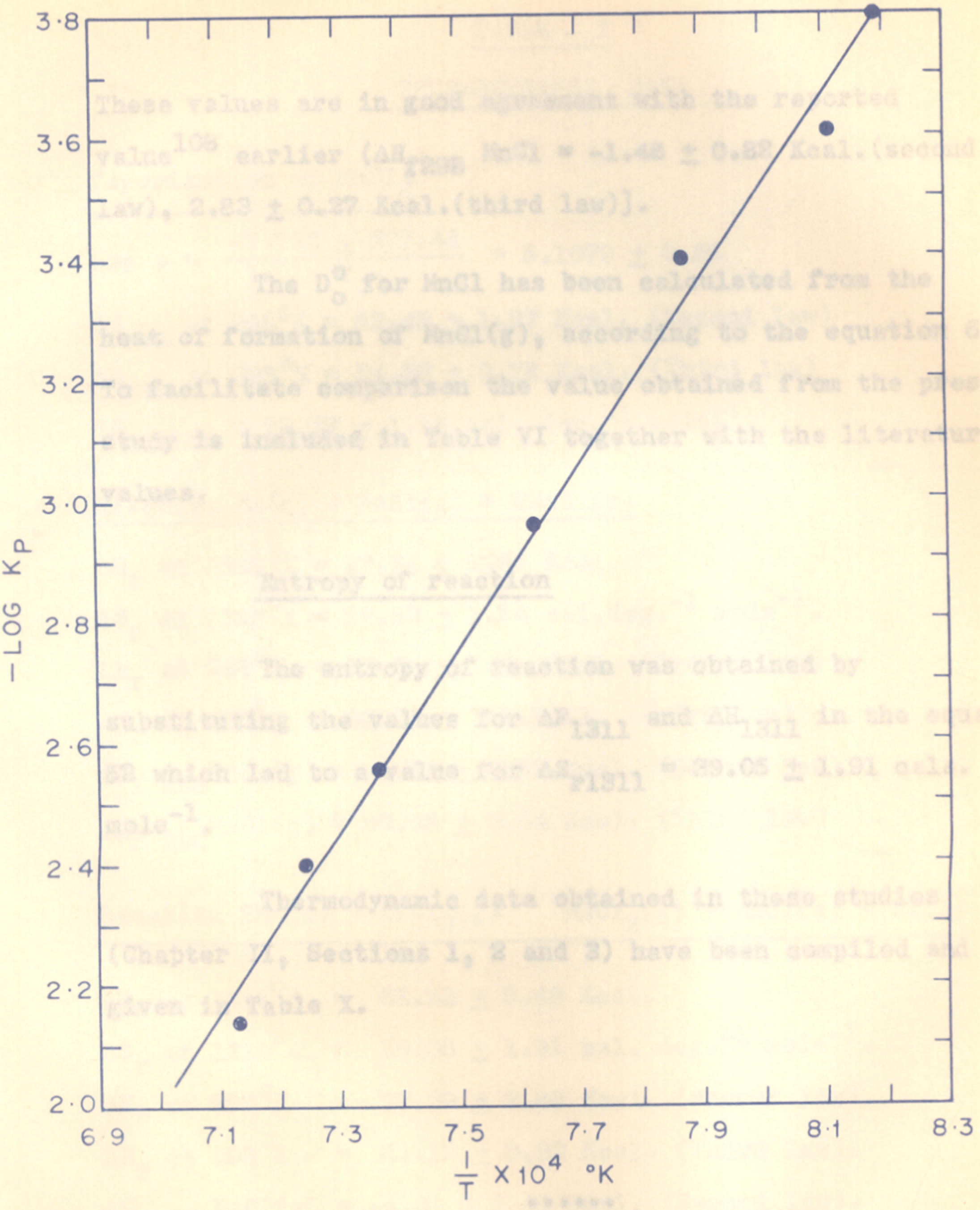


FIG. 7 PLOT OF LOG K_P VS $^1/_T \times 10^4$ FOR THE REACTION $2Mn(c) + AlCl_3(g) = MnCl_2(g) + MnCl(g) + Al(l)$.

These values are in good agreement with the reported value[108] earlier (ΔH_{f298} MnCl = -1.48 ± 0.82 Kcal.(second law), 2.83 ± 0.27 Kcal.(third law)].

The D_o^o for MnCl has been calculated from the heat of formation of MnCl(g), according to the equation 62. To facilitate comparison the value obtained from the present study is included in Table VI together with the literature values.

Entropy of reaction

The entropy of reaction was obtained by substituting the values for ΔF_{1311} and ΔH_{1311} in the equation 52 which led to a value for $\Delta S_{r1311} = 39.05 \pm 1.91$ cals. deg.$^{-1}$ mole^{-1}.

Thermodynamic data obtained in these studies (Chapter II, Sections 1, 2 and 3) have been compiled and given in Table X.

……

TABLE - X

THERMODYNAMIC DATA

Vaporization of $MnCl_2$

$$\text{Log } p = \frac{-7.729 \pm 277.48}{T} + 5.1079 \pm 0.25$$

ΔH_{vap} at 298°K = 52.42 ± 1.27 Kcal. (Second law)

ΔH_{vap} at 298°K = 54.52 ± 0.78 Kcal. (Third law)

$\Delta S_{r\ 1106}$ = 23.37 ± 1.16 cal. deg.$^{-1}$ mole.$^{-1}$

Reaction $Mn(c) + MnCl_2(g) \rightleftarrows 2MnCl(g)$

ΔH_r at 1328°K = 47.34 ± 1.64 Kcal.

ΔS_r at 1328°K = 22.83 ± 1.24 cal.deg.$^{-1}$ mole^{-1}.

ΔH_r at 298°K = 57.64 ± 1.64 Kcal. (Second law)

ΔH_r at 298°K = 66.35 ± 1.1 Kcal. (Third law)

$\Delta H_{f\ 298}$ MnCl(g) = -1.53 ± 0.82 Kcal. (Second law)

$\Delta H_{f\ 298}$ MnCl(g) = +2.83 ± 0.54 Kcal. (Third law)

Reaction $2Mn(c) + AlCl_3(g) \quad MnCl_2(g) + MnCl(g) + Al(l)$

ΔH_r at 1311°K = 68.93 ± 2.49 Kcal.

ΔS_r at 1311°K = 39.05 ± 1.91 cal. deg.$^{-1}$ mole^{-1}.

ΔH_r at 298°K = 77.39 ± 2.49 Kcal. (Second law).

ΔH_r at 298°K = 81.12 ± 0.93 Kcal. (Third law).

$\Delta H_{f\ 298}$ MnCl(g) = -4.01 ± 2.49 Kcal. (Second law).

$\Delta H_{f\ 298}$ MnCl(g) = -0.27 ± 0.68 Kcal. (Third Law).

CHAPTER - III

REACTIONS OF A METAL HALIDE WITH METAL OXIDES AT HIGH TEMPERATURES

1) REACTION OF $AlCl_3(g)$ WITH $Mn_3O_4(c)$
2) REACTION OF $AlCl_3(g)$ WITH $CoO(c)$
3) REACTION OF $AlCl_3(g)$ WITH $Fe_2O_3(c)$

REACTIONS OF A METAL HALIDE WITH METAL OXIDES AT HIGH TEMPERATURES

3.1. INTRODUCTION

It is known that whenever a metal halide reacts with an oxide of a divalent metal there is the possibility of the formation of the corresponding oxyhalide according to the equation[11]

$$MeO(c) + RX_n(g) = MeX_2(g) + ROX_{n-2}(g) \qquad ...(76)$$

A metal halide like aluminium chloride reacts in a variety of ways to form aluminium oxychloride. In each of the following cases AlOCl(solid) is one of the products of the reaction:

(A) High temperature gaseous hydrolysis

$$AlCl_3 + H_2O = 2AlOCl + 2HCl \qquad ...(77)$$

(B) Direct oxidation of AlCl$_3$[109]

$$2AlCl_3 + O_2 = 2AlOCl + 2Cl_2 \qquad ...(78)$$

(C) Oxyhalide reactions

$$AlCl_3 + FeOCl \rightleftharpoons AlOCl + FeCl_3 \qquad ...(79)$$

(D) Oxyhydroxy reaction

$$AlO(OH) + AlCl_3 \rightleftharpoons 2AlOCl + HCl \qquad ...(80)$$

(E) Oxide reactions

$AlCl_3$ + metal oxide = AlOCl + metal chloride.(81)

$AlCl_3$+ metal oxide = AlOCl + metal oxychloride(82)

$AlCl_3$ + metal oxide = AlOCl + metal chloride..(83
+ Cl_2

Schäfer et.al.[110,111] have shown that aluminium oxychloride can be prepared at elevated temperatures by the reaction of $AlCl_3$ with a number of oxides. These include CaO and MgO[112], Bi_2O_3, Sb_2O_3 and ZnO[110], Fe_2O_3, As_2O_3, TiO_2, Nb_2O_5 and Ta_2O_5[111]. In all these reactions the by-product is the corresponding metal chloride, in which the metal has the same oxidation state as the metal originally had. Some oxides react according to the equation 82, in that the by-product is another oxychloride. Examples of this type are SO_2 which forms $SOCl_2$, V_2O_5, which forms $VOCl_3$ and WO_3 which forms $WOCl_4$. Antimony pentoxide reacts according to the reaction given by equation 83 forming the trivalent $SbCl_3$ and Cl_2. The oxyhalides of Al were prepared by Hagenmuller[113] by reacting Al_2O_3 with excess of $AlCl_3$ in sealed tubes at 250-400°. Jean Rouxel[114] obtained pure AlOCl by heating $AlCl_3$ with As_2O_3 in sealed glass tube at 360°. Two excellent reviews are available on the syntheses, stabilities and properties of various oxyhalides by Dehnicke[115] and Siegel[116].

Fischer and Gewehr[117] claimed to have detected the presence of gaseous AlOCl by vapour pressure measurements when alumina was reacted with chlorine at 1250°C. The existence of some of the gaseous oxyhalides of light metals like boron, gallium and aluminium[118-123] has been proved by effusion and mass spectrometry. Greenbaum et.al.[124] have reported the existence of gaseous AlOCl at 2400°K and claimed to be the first to determine its heat of formation experimentally using the molecular effusion method in the study of the reaction

$$1/3\ Al_2O_3(l) + 1/3\ AlCl_3(g) = AlOCl(g) \qquad ...(84)$$

It is obvious from the above information that though a good bit of study has been done on solid AlOCl, yet there have been few attempts to study the thermodynamic properties of gaseous AlOCl. Therefore, it was thought worthwhile to investigate the reaction of $AlCl_3(g)$ with transition metal oxides viz. Mn_3O_4, CoO and Fe_2O_3 at high temperatures employing transpiration technique and to determine the heat of formation of AlOCl(g)

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

SECTION - 1

REACTION OF $AlCl_3(g)$ WITH $Mn_3O_4(c)$

3.1.1. EXPERIMENTAL

(A) Materials

Mn_3O_4 - Reagent grade manganese dioxide supplied by E. Merck was heated at about 1000°C in argon atmosphere for several hours to produce Mn_3O_4 ($MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4$[125,126]) and analysed chemically by the standard methods for manganese. Spectrographic analysis revealed the presence of traces of Fe, Al, Ni and Si. X-ray powder pattern of the solid showed the presence of Mn_3O_4 only.

Aluminium trichloride - 99.9% pure $AlCl_3$ (as described earlier) was used.

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

(B) Apparatus and procedure

The experimental set up and the procedure were similar to that described in Chapter II, Section 3. The carrier gas saturated with $AlCl_3$ vapour was allowed to react with $Mn_3O_4(c)$ under equilibrium conditions. The experiment was carried out for a definite period of time and the heating of $AlCl_3$ was stopped thereby arresting the reaction. The system was allowed to cool in argon atmosphere and the boats containing Mn_3O_4 and $AlCl_3$ were weighed. The products in the boat after the experimental run were identified by X-ray analysis and the amount of Mn_3O_4 taking part in the reaction was determined by the chemical analysis of the products in the boat.

The gaseous products of the reaction carried away by the argon gas were condensed on a silica cold finger. Since in the preliminary experiments the evolution of chlorine gas was also observed, arrangements were made to collect the gases and estimate chlorine gas quantitatively by absorbing it in a trap containing a concentrated solution of potassium iodide (the liberated iodine being estimated by standard analytical methods).

3.1.2. IDENTIFICATION OF THE PRODUCTS

The residue in the boat was examined by studying the X-ray powder patterns of the solids. A sample of the residue ground to fine size was introduced in a glass capillary tube and the photograph of the diffraction pattern was taken (radiation: molybdenum $K\alpha\lambda = 0.70926^{o}$). The powder pattern showed the presence of Mn_3O_4 and α-Al_2O_3. The Mn_3O_4 observed was due to the unreacted material. The X-ray data is given in Table XI in which the prominent 'd' values for Mn_3O_4 and Al_2O_3 are shown for comparison with their standard patterns[127,128].

TABLE - XI

PROMINENT X-RAY DIFFRACTION LINES FOR Mn_3O_4 AND Al_2O_3

Mn_3O_4(c) Radiation : Molybdenum Ka

Al_2O_3(c) Radiation : Cu K

Mn_3O_4(c)				Al_2O_3(c)			
ASTM Index*		Experimental		Standard**		Experimental	
dÅ	Intensity	dÅ	Intensity	dÅ	Intensity	dÅ	Int.
4.92	20	-	-	3.48	8	-	-
3.08	31	3.09	M	2.55	9	2.583	M
2.87	8	2.90	W	2.38	7	2.40	M
2.75	63	2.78	S	2.08	10	2.096	S
2.48	100	2.50	S	1.74	8	1.751	M
2.36	13	2.38	M	1.60	10	1.609	S
2.03	15	2.056	M	1.54	2	1.531	W
1.79	18	1.805	M	1.51	4	-	-
1.70	5	-	-	1.40	7	1.424	S
1.64	5	-	-	1.369	10	1.373	S
1.57	50	1.585	S	1.335	1	-	-
1.54	50	1.548	S	1.272	1	-	-
1.47	3	-	-	1.235	6	1.242	M
1.44	18	1.448	M	1.187	3	1.195	W
1.38	4	-	-	1.156	1	-	-
1.34	8	1.35	W	1.145	3	-	-
1.30	3	-	-	1.123	3	1.130	W
1.28	13	1.285	W	1.097	4	1.083	W
1.24	4B	1.231	W	1.076	4	-	-
1.19	5B	1.185	W	1.042	5	1.04	W
1.12	4	1.129	W	1.016	2	-	-
				0.996	5	0.999	W

* ASTM Index No: 1-1127.

** Ref. No. 128.

The identification of the gaseous products was carried out by condensing them on a cold finger. Light pink crystals which were clearly visible on the cold finger indicated that $MnCl_2$ was one of the products. The cold finger with the condensate was heated at about 800°C under reduced pressure (2-3 mm. Hg) when both the halides $AlCl_3$ and $MnCl_2$ were sublimed off leaving behind white powder on the cold finger. X-ray and chemical analysis of the powder showed it to be alumina. It is possible that Al_2O_3 was formed due to the dissociation of AlOCl(g) according to the equation

$$3AlOCl(g) = Al_2O_3(c) + AlCl_3(g) \qquad \ldots(85)$$

3.1.3. ANALYSIS OF THE PRODUCTS IN THE BOAT

The alumina obtained in the boat together with excess oxide was finely ground. The fine powder was fused with potassium-pyrosulphate (ratio $K_2S_2O_8$: substance = 20:1) in a silica crucible. After the substance was fused completely, the crucible with the contents was cooled and the solid mass was treated with 1N sulphuric acid. Aluminium in this was determined gravimetrically as alumine by the standard method[96]. The filtrate remaining after the separation of aluminium hydroxide was analysed for manganese by standard phosphate method. By deducting the quantity of Al_2O_3 obtained from the residue in the boat, the weight of unreacted Mn_3O_4 was obtained. Mn_3O_4 reacted was calculated from the initial weight of Mn_3O_4 and the weight of unreacted Mn_3O_4. Further, the amount of Cl_2 absorbed in potassium iodide solution was titrated against standard hyposolution and the quantity of Cl_2 liberated was calculated. The analysis of chlorine showed that for every mole of oxide reacted one mole of chlorine was evolved.

3.1.4. TREATMENT OF THE DATA

Considering alumina, manganese chloride, aluminium oxychloride and chlorine as the reaction products and from the quantitative estimation of alumina and chlorine, the reaction may be represented as:

$$Mn_3O_4(c) + 3.5\,AlCl_3(g) = \frac{1}{2}Al_2O_3(c) + 2.5\,AlOCl(g) + 3MnCl_2(g) + Cl_2(g) \quad \ldots(86)$$

The vapour pressures of $MnCl_2(g)$, $AlOCl(g)$, $Cl_2(g)$ and $AlCl_3(g)$ were calculated from the experimentally determined weight loss of Mn_3O_4 in the reaction 86. Assuming that the ideal gas law holds good in the equilibrium, the partial pressures of the various components were calculated as follows:

$$P_{MnCl_2} = 3 \times n\,Mn_3O_4 \times RT_r/V_r \quad \ldots(87)$$

$$P_{AlOCl} = 2.5 \times n\,Mn_3O_4 \times RT_r/V_r \quad \ldots(88)$$

$$P_{Cl_2} = n\,Mn_3O_4 \times RT_r/V_r \quad \ldots(89)$$

$$P_{AlCl_3} = (n\,AlCl_3 - 3.5\,n\,Mn_3O_4)\,RT_r/V_r \quad \ldots(90)$$

where P_{MnCl_2}, P_{AlOCl}, P_{Cl_2} and P_{AlCl_3} denote the partial pressures of the respective components and V_r represents the volume of flow gas passed at the room temperature, T_r and R being the gas constant. n Mn_3O_4 and n $AlCl_3$ denote the number of moles of the respective components.

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

$$K_p = \frac{(P^3_{MnCl_2})\,(P^{2.5}_{AlOCl})(P_{Cl_2})}{(P^{3.5}_{AlCl_3})} \qquad \ldots(91)$$

3.1.5. RESULTS

The experimental results together with the calculated vapour pressures of $MnCl_2$, AlOCl, Cl_2 and $AlCl_3$ and equilibrium constants are presented in Table XII. The free energies and heats of reaction at various temperatures are calculated from the equation

$$\Delta F^o = -RT\ln K \qquad \ldots(28)$$

The free energy functions for products and reactants are taken from Kelley[100], 'JANAF' tables[107] and Brewer and Somayajulu[99]. The calculated free energies and the third law heats for the reaction 86 have been summarized in table XIII.

TABLE - XII

TRANSPIRATION DATA FOR THE REACTION

$Mn_3O_4(c) + 3.5AlCl_3(g) = \frac{1}{2}Al_2O_3(c) + 2.5AlOCl(g) + 3MnCl_2(g) + Cl_2(g)$ AND EQUILIBRIUM CONSTANTS

Temp. ^{o}K	Flow Lit./ hour	$AlCl_3$ trans- ported g	Mn_3O_4 reacted g	P_{MnCl_2} atm.	P_{AlOCl} atm.	P_{Cl_2} atm.	P_{AlCl_3} atm.10^{-2}	K_p
1213	6.84	1.6353	0.1208	5.6625×10^{-3}	4.7188×10^{-3}	1.8875×10^{-3}	3.7232	5.2712×10^{-11}
1243	7.40	2.6140	0.2401	1.0403×10^{-2}	8.6692×10^{-3}	3.4676×10^{-3}	5.2625	8.1637×10^{-10}
1268	7.40	2.5016	0.2754	1.1932×10^{-2}	9.9438×10^{-3}	3.9775×10^{-3}	4.8055	2.7396×10^{-9}
1294	7.60	2.7160	0.3489	1.4719×10^{-2}	1.2266×10^{-2}	4.9064×10^{-3}	4.8347	1.0506×10^{-8}
1316	7.20	3.0653	0.4763	2.1214×10^{-2}	1.7678×10^{-2}	7.0710×10^{-3}	5.3308	8.0180×10^{-8}
1357	9.00	2.2053	0.5104	1.8183×10^{-2}	1.5152×10^{-2}	6.0610×10^{-3}	2.3710	5.0160×10^{-7}
1373	7.60	2.1011	0.5018	2.1169×10^{-2}	1.7641×10^{-2}	7.0566×10^{-3}	2.5990	9.7807×10^{-7}
1388	6.90	2.5160	0.5809	2.6994×10^{-2}	2.2495×10^{-2}	8.9979×10^{-3}	3.5360	1.6140×10^{-6}
1403*	3.90	1.9330	0.4268	3.5088×10^{-2}	2.9240×10^{-2}	1.1696×10^{-2}	4.9945	2.6530×10^{-6}
1433*	3.70	1.6592	0.4688	4.0624×10^{-2}	3.3853×10^{-2}	1.3541×10^{-2}	3.4834	2.4219×10^{-5}

* Reactions were carried out for 1 hour, others for 2 hours.

TABLE - XIII

FREE ENERGY AND THE THIRD LAW HEATS FOR THE REACTION SHOWN IN TABLE XII

Temp. ^{o}K	$-\log K_p$	$-R\ln K_p$	$-RT\ln K_p$ Kcal.	$-\Delta\left(\frac{F_T - H_{298}}{T}\right)$	ΔH_{r298} Kcal.	ΔH_{f298} AlOCl(g) Kcal.
1213	10.2781	47.0305	57.0479	126.170	210.09	-91.18
1243	9.0881	41.5853	51.6905	126.100	208.43	-91.85
1268	8.5622	39.1789	49.6788	126.065	209.53	-91.41
1294	7.9783	36.5071	47.2402	125.980	210.26	-91.12
1316	7.0960	32.4698	42.7302	125.835	208.33	-91.89
1357	6.2997	28.8260	39.1169	125.680	209.53	-91.41
1373	6.0097	27.4992	37.7564	125.645	210.27	-91.11
1388	5.7921	26.5030	36.7862	125.580	211.09	-90.78
1403	5.5763	25.5160	35.7989	125.505	211.88	-90.47
1433	4.6158	21.1209	30.2662	125.260	209.76	-91.32
					Avr. 209.92 ± 1.96	Avr -91.25 ± 0.78

Employing Vant Hoff's equation, the heat of reaction ΔH_r has been determined from the plot of logarithm of the equilibrium constant vs the reciprocal of the absolute temperature (Fig. 8). The slope of the line obtained by the method of least squares gave the heat of reaction $\Delta H_r = 193.92 \pm 5.88$ Kcal. This value of ΔH_r represents the mean value over the temperature range studied and does not take into account the effect of C_p.

From the functions cited in the 'JANAF' tables[107] and Kelley[100] and applying Kirchoff's Law, ΔH_{r298} for the reaction 86 becomes 208.88 ± 5.88 Kcal., which is in good agreement with the corresponding third law value 209.92 ± 1.96 Kcal.

Heat of formation of AlOCl(g)

The second law heat of reaction permits the calculation of the heat of formation of AlOCl from the equation

$$\Delta H^o_{r298} = \Delta H_{f298} \text{ Products} - \Delta H_{f298} \text{ reactants} \qquad \ldots(92)$$

$$= \Delta H_f[1/2\ Al_2O_3(c) + 2.5 AlOCl(g) + 3MnCl_2(g) + Cl_2(g)]$$

$$-\Delta H_f[Mn_3O_4(c) + 3.5 AlCl_3(g)] \qquad \ldots(93)$$

$$= 208.88 \pm 5.88 = 438.05 + 2.5\ \Delta H_{f298}\ AlOCl(g) \qquad \ldots(94)$$

$$\therefore \Delta H_{f298}\ AlOCl(g) = -91.67 \pm 2.35 \text{ Kcal.} \qquad \ldots(95)$$

The corresponding third law value gives -91.25 ± 0.78 Kcal. The ΔH_{f298} values for $AlCl_3(g)$, $Al_2O_3(c)$ were taken from

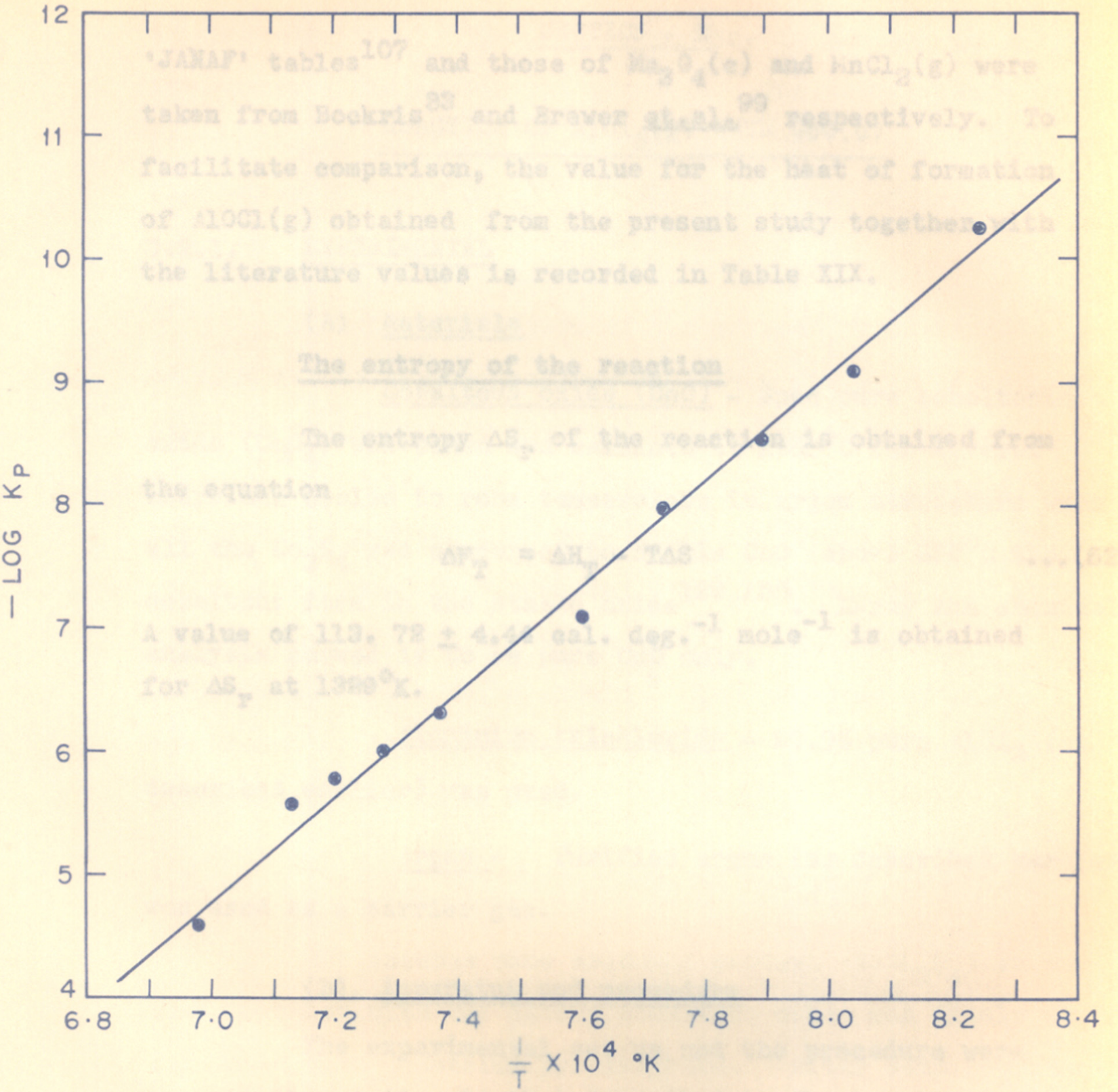


FIG. 8. PLOT OF LOG K_P VS $1/T \times 10^4$ FOR THE REACTION $Mn_3O_4(c) + 3{\cdot}5\ AlCl_3(g) = \frac{1}{2}\ Al_2O_3(c) + 2{\cdot}5\ AlOCl\ (g) + 3MnCl_2(g) + Cl_2(g)$.

'JANAF' tables[107] and those of $Mn_3O_4(c)$ and $MnCl_2(g)$ were taken from Bockris[33] and Brewer et.al.[99] respectively. To facilitate comparison, the value for the heat of formation of AlOCl(g) obtained from the present study together with the literature values is recorded in Table XIX.

The entropy of the reaction

The entropy ΔS_r of the reaction is obtained from the equation

$$\Delta F_T = \Delta H_T - T\Delta S \qquad ...(52)$$

A value of 113. 72 ± 4.44 cal. deg.$^{-1}$ mole^{-1} is obtained for ΔS_r at 1329°K.

SECTION - 2

REACTION OF $AlCl_3(g)$ WITH CoO(c)

3.2.1. EXPERIMENTAL

(A) Materials

Cobaltous oxide (CoO) - Spec pure cobaltosic oxide (Co_3O_4) was taken and calcined at 1050°C for several hours and cooled to room temperature in argon atmosphere when all the Co_3O_4 was converted to stable CoO (above 850°C the cobaltous form is the stable oxide[129,130]). X-ray and chemical analysis showed it to be pure CoO only.

Aluminium trichloride - 99.9% pure $AlCl_3$ (as described earlier) was used.

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

(B) Apparatus and procedure

The experimental set up and the procedure were essentially similar to that described in Chapter II, Section 3.

3.2.2. IDENTIFICATION OF THE PRODUCTS

The residue in the boat was examined by studying X-ray powder pattern and chemical analysis. X-ray powder pattern showed the presence of cobalt aluminate spinel ($CoAl_2O_4$). The 'd' lines for CoO(c) indicated the presence of unreacted CoO. Those corresponding to alumina phase were not observed indicating its absence. The spinel could be identified by comparing the powder patterns of the residue with that given by the N.B.S.[131]. The comparison of the pattern is given in Table XIV.

The identification of the gaseous products was carried out by condensing them on a cold finger. Fine blue crystals of $CoCl_2$ were observed indicating it to be one of the reaction products. The cold finger with the condensate was heated under reduced pressure (about 800°C and 2-3 mm. Hg), until $AlCl_3$ and $CoCl_2$ were completely sublimed off. A white residue was left behind, which on X-ray and chemical analysis was found to be alumina. The presence of Al_2O_3 may be due to the disproportionation of AlOCl(g) according to the reaction (equation 85).

3.2.3. ANALYSIS OF THE PRODUCTS IN THE BOAT

The intense blue coloured product ($CoAl_2O_4$) in the boat together with the excess cobaltous oxide was finely ground and fused with potassium pyrosulphate. After complete fusion, the mass was extracted with dilute sulphuric acid and was made to a definite volume. A portion of it was taken and aluminium was determined gravimetrically as alumina. The filtrate after the separation of aluminium hydroxide was estimated for

TABLE - XIV

PROMINENT X-RAY DIFFRACTION LINES OF $CoAl_2O_4$ FORMED IN THE REACTION

Radiation : Fe 1.9360A

$CoAl_2O_4(c)$

Standard*		Experimental	
dÅ	Intensity	dÅ	Intensity
2.864	66	2.8387	S
2.443	100	2.4263	VS
2.026	17	1.9991	M
1.8608	5	-	-
1.6541	16	1.6390	M
1.5602	34	1.5408	S
1.4324	41	1.4177	S
1.3716	1	1.3771	W
1.2821	7	-	-
1.2360	2	1.2234	W
1.0826	2	1.0752	W
1.0551	3	1.0470	W
1.0131	1		
0.9547	2		
~~0.9547~~	~~2~~		
0.9355	2		

* Ref. No. 131

cobalt by standard methods[96]. From the alumina obtained, the corresponding cobalt aluminate was calculated and the amount deducted from the total weight of the substance in the boat after the experiment. This gave the weight of unreacted CoO. CoO reacted was calculated from the initial weight of CoO and the weight of unreacted CoO.

3.2.4. TREATMENT OF THE DATA

Considering cobalt aluminate, cobalt chloride and AlOCl(g) as the products and from the quantitative estimation of $CoAl_2O_4$, the following stoichiometric reaction can be written:

$$6CoO(c) + 4AlCl_3(g) = CoAl_2O_4(c) + 5CoCl_2(g) + 2AlOCl(g) \quad \ldots(96)$$

The vapour pressures of $CoCl_2(g)$, AlOCl(g) and $AlCl_3(g)$ were calculated from the experimentally determined weight loss data of CoO in the reaction 96. The partial pressures of the various components were calculated as follows:

$$P_{CoCl_2} = 5/6 \times n\ CoO \times RT_r/V_r \quad \ldots(97)$$

$$P_{AlOCl} = 2/6 \times n\ CoO \times RT_r/V_r \quad \ldots(98)$$

$$P_{AlCl_3} = (n\ AlCl_3 - 4/6\ n\ CoO)\ RT_r/V_r \quad \ldots(99)$$

where P_{CoCl_2}, P_{AlOCl} and P_{AlCl_3} denote the partial pressures of the respective components and V_r represents the volume of flow gas passed at the room temperature, T_r and R being the gas constant. n CoO and n $AlCl_3$ denote the number of moles of the respective components.

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

$$K_p = \frac{(P^5_{CoCl_2})(P^2_{AlOCl})}{(P^4_{AlCl_3})} \qquad ...(100)$$

3.2.5. RESULTS

The experimental results together with the calculated vapour pressures of $CoCl_2$, AlOCl and $AlCl_3$ and equilibrium constants are summarized in Table XV. Employing the Vant Hoff's equation the heat of reaction ΔH_r has been determined from the plot of log K_p vs $1/T$ (Fig. 9). The slope of the line obtained by the method of least squares gave the heat of reaction $\Delta H_r = 153.97 \pm 4.0$ Kcal. This value of ΔH_r represents the mean over the temperature range studied and does not take into account the effect of C_p. From the functions cited by Kelley[100] and 'JANAF' tables[107] and by the application of Kirchoff's law, ΔH_{r298} for the reaction 96 was found to be 172.12 ± 4.0 Kcal. [(C_p value for $CoCl_2$(g) was taken as 14 cal.deg.$^{-1}$ mole^{-1}. The heat capacities of $CoAl_2O_4$(c) was taken as the sum of the heat capacities of CoO(c) and Al_2O_3(c)].

TABLE - XV

TRANSPIRATION DATA FOR THE REACTION $6CoO(c) + 4AlCl_3(g) = CoAl_2O_4(c) + 5CoCl_2(g) + 2AlOCl(g)$ AND EQUILIBRIUM CONSTANTS

Temp. °K	Flow Lit./ hour	$AlCl_3$ transported g	CoO reacted g	P_{CoCl_2} atm. x 10^{-2}	P_{AlOCl} atm.	P_{AlCl_3} atm. x 10^{-2}	K_p	$-\text{Log } K_p$
1124	3.50	1.0707	0.1401	1.0884	4.3536×10^{-3}	4.7388	5.7406×10^{-10}	9.2410
1148	3.90	1.0902	0.1703	1.1873	4.7493×10^{-3}	4.1756	1.7523×10^{-9}	8.7565
1172	3.70	1.5281	0.2649	1.9467	7.7868×10^{-3}	6.0158	1.2956×10^{-8}	7.8874
1214	3.55	1.5559	0.3167	2.4257	9.7030×10^{-3}	6.0965	5.7336×10^{-8}	7.2415
1245	3.55	1.1759	0.3215	2.4625	9.8501×10^{-3}	4.1038	3.0943×10^{-7}	6.5094
1263	3.80	1.4643	0.4408	3.1541	1.2616×10^{-2}	4.5429	1.1673×10^{-6}	5.9328
1297	3.70	1.5326	0.5130	3.7699	1.5079×10^{-2}	4.5791	3.9367×10^{-6}	5.4048
1333	3.70	1.4476	0.5859	4.3057	1.7223×10^{-2}	3.7293	2.2728×10^{-5}	4.6434
1361*	1.85	0.6508	0.3122	4.5886	1.8354×10^{-2}	2.7796	1.1484×10^{-4}	3.9400

*The experiment was carried out for 1/2 hour, others for 1 hour.

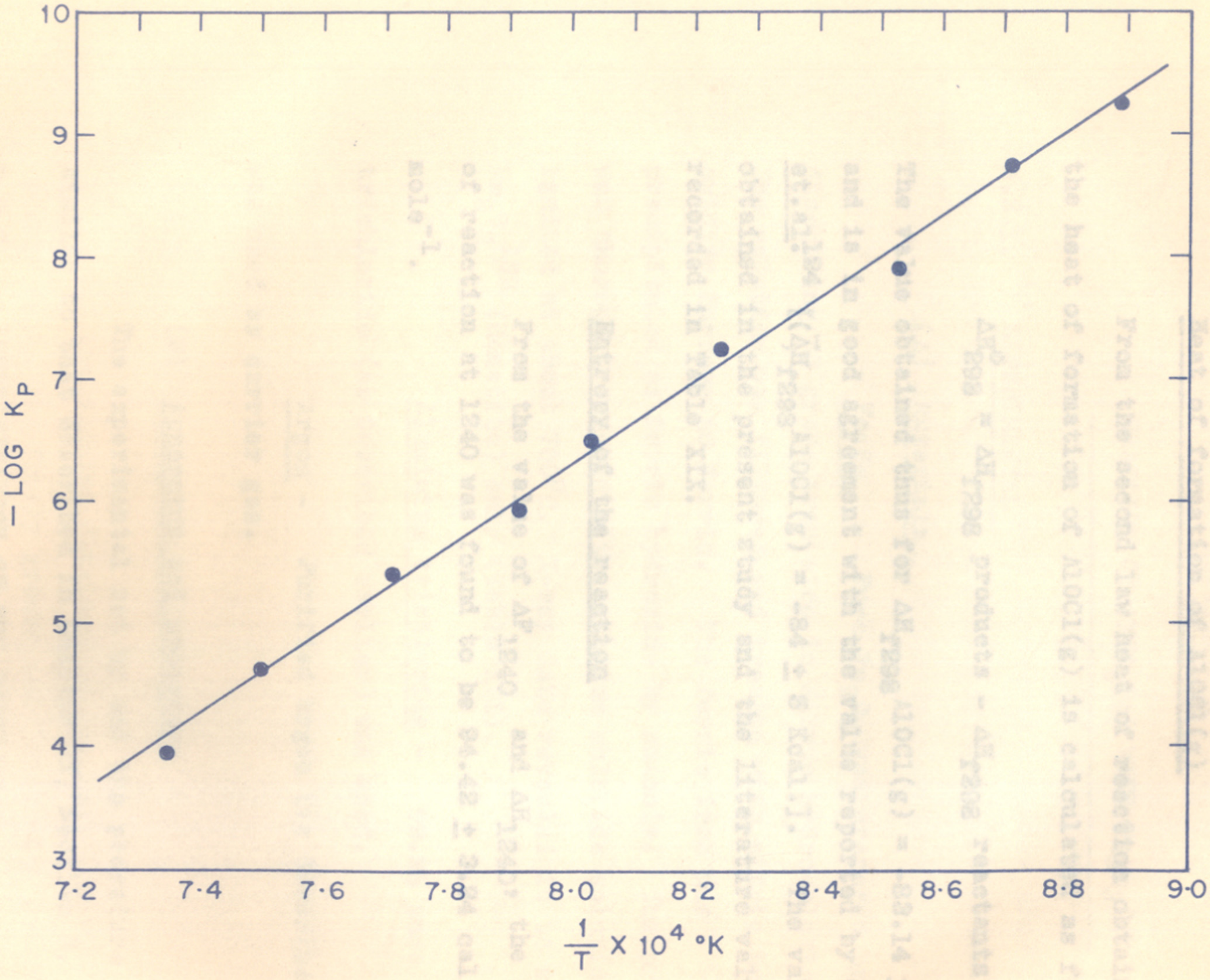


FIG. 9. PLOT OF LOG K_P VS $^1/_T \times 10^4$ FOR THE REACTION

$6\,CoO(c) + 4\,AlCl_3(g) = CoAl_2O_4(c) + 2\,AlOCl\,(g) + 5\,CoCl_2(g)$.

Heat of formation of AlOCl(g)

From the second law heat of reaction obtained, the heat of formation of AlOCl(g) is calculated as follows

$$\Delta H^{o}_{298} = \Delta H_{f298} \text{ products} - \Delta H_{f298} \text{ reactants} \quad \ldots(92)$$

The value obtained thus for ΔH_{f298} AlOCl(g) = -83.14 ± 2.0 Kcal. and is in good agreement with the value reported by Greenbaum et.al.[124] [($\bar{\Delta} H_{f298}$ AlOCl(g) = -84 ± 5 Kcal.]. The value obtained in the present study and the literature values are recorded in Table XIX.

Entropy of the reaction

From the value of ΔF_{1240} and ΔH_{1240}, the entropy of reaction at 1240 was found to be 94.42 ± 3.24 cal.deg.$^{-1}$ mole^{-1}.

SECTION - 3

REACTION OF $AlCl_3(g)$ WITH $Fe_2O_3(c)$

3.3.1. EXPERIMENTAL

(A) Materials

Fe_2O_3 - Pure Fe_2O_3 was prepared by dissolving AR grade iron wire in dilute hydrochloric acid. The solution was filtered and treated with nitric acid to oxidize ferrous to ferric. The ferric iron was precipitated as ferric hydroxide by ammonia. The precipitate was thoroughly washed with ammonium chloride solution and ignited at about 700°C. X-ray data revealed it to be Fe_2O_3[132] (Hematite) only (Table XVI).

Aluminium trichloride - 99.9% pure aluminium trichloride (as described earlier) was used.

Argon - Purified argon (as described earlier) was used as carrier gas.

(B) Apparatus and procedure

The experimental set up and the procedure were similar to that described in Chapter II, Section 3.

3.3.2. IDENTIFICATION OF THE PRODUCTS

The residue in the boat was examined by studying the X-ray powder patterns of the solids. X-ray data presented in Table XVI showed the presence of Fe_2O_3 and αAl_2O_3. The Fe_2O_3 observed was due to the unreacted material.

In the preliminary experiments, the outgoing gases when tested revealed traces of chlorine which may be due to the dissociation of $FeCl_3$ as the temperatures are high. The identification of the gaseous products were carried out by condensing them on the cold finger. Chemical analysis of the condensed iron chloride on cold finger showed the existence of ferric state. The cold finger with the condensate was heated under reduced pressure when all $AlCl_3$ and $FeCl_3$ were sublimed off leaving behind white solid on the cold finger. X-ray and chemical analysis of the material showed it to be Al_2O_3. The presence of Al_2O_3 may be due to the disproportionation of AlOCl(g) according to the reaction (equation 85).

It may be mentioned that no iron deposit was observed on the cold finger indicating the absence of FeOCl and FeCl.

3.3.3. ANALYSIS OF THE PRODUCTS

The alumina obtained in the boat together with excess Fe_2O_3 was finely ground and fused with potassium pyrosulphate. After the fusion is complete, the mass is extracted with dilute sulphuric acid and made to a definite volume. A portion of the aliquot was taken, precipitated

TABLE - XVI

PROMINENT X-RAY DIFFRACTION LINES FOR Fe_2O_3 AND Al_2O_3*

Radiation : Cu K (1.5405A)

$Fe_2O_3(c)$**

Experimental		ASTM Index	
dÅ	Intensity	dÅ	Intensity
2.744	S	3.68	18
2.688	S	2.69	100
2.552	S	2.51	75
2.515	S	2.20	18
2.213	W	1.84	63
1.852	M	1.69	63
1.836	S	1.60	13
1.708	M	1.49	50
1.695	S	1.45	50
1.484	S	1.35	3
1.455	S	1.31	18
1.309	W	1.26	13
1.256	W	1.23	3
1.142	M	1.19	8
1.104	M	1.16	5
1.058	M	1.14	13
0.961	M	1.10	10
0.951	M	1.06	8
		0.96	10

* The d values obtained for alumina were the same as given in Table XI.

** ASTM Index No: 1-1053.

with sodium hydroxide and iron was estimated as ferric oxide by standard methods of analysis[96]. The filtrate after the separation of ferric hydroxide is estimated for alumina by standard methods of analysis. By deducting the quantity of Al_2O_3 obtained from the residue in the boat, the weight of unreacted Fe_2O_3 was obtained. Fe_2O_3 reacted was calculated from the initial weight of Fe_2O_3 and the weight of unreacted Fe_2O_3.

3.3.4. TREATMENT OF THE DATA

Considering alumina, ferric chloride and aluminium oxychloride as the reaction products and from the quantitative estimation of alumina, the reaction can be represented as

$$2Fe_2O_3(c) + 5AlCl_3(g) = Al_2O_3(c) + 3AlOCl(g) + 4FeCl_3(g) \quad \ldots(101)$$

The vapour pressures of $AlOCl(g)$, $FeCl_3(g)$ and $AlCl_3(g)$ were calculated from the experimentally determined weight loss data of Fe_2O_3 in the reaction 101. The partial pressures of the various components were calculated as follows:

$$P_{AlOCl} = 3/2 \times n\ Fe_2O_3 \times RT_r/V_r \quad \ldots(102)$$

$$P_{FeCl_3} = 4/2 \times n\ Fe_2O_3 \times RT_r/V_r \quad \ldots(103)$$

$$P_{AlCl_3} = (n\ AlCl_3 - 5/2\ n\ Fe_2O_3)\ RT_r/V_r \quad \ldots(104)$$

where P_{AlOCl}, P_{FeCl_3}, and P_{AlCl_3} denote the partial pressures of the respective components and V_r represents the volume of flow gas passed at the room temperature T_r and R being the gas constant. nFe_2O_3 and $n\ AlCl_3$ denote the number of moles of the respective components.

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

$$K_p = \frac{(P^4_{FeCl_3})(P^3_{AlOCl})}{(P^5_{AlCl_3})} \qquad \ldots(105)$$

3.3.5. RESULTS

The experimental results together with the calculated vapour pressures of $FeCl_3$, AlOCl and $AlCl_3$ are recorded in Table XVII. Employing the Vant Hoff's equation, the heat of reaction ΔH_r has been determined from the plot of log K_p vs 1/T (Fig. 10). The slope of the line obtained by the method of least squares gave the heat of reaction $\Delta H_r = 113.45 \pm 4.76$ Kcal. This value of ΔH_r represents the mean value over the temperature studied and does not take into account the effect of C_p. From the functions cited by Kelley[100] and 'JANAF' tables[107] and by the application of Kirchoff's law, ΔH_{r298} for the reaction 101 becomes 133.68 ± 4.76 Kcal.

Heat of formation of AlOCl

The heat of formation of AlOCl(g) has been calculated from the second law heat of reaction, which gave a value of -80.41 ± 1.59 Kcal. The heat of formation

TABLE - XVII

TRANSPIRATION DATA FOR THE REACTION $2Fe_2O_3(c) + 5AlCl_3(g) = Al_2O_3(c) + 3AlOCl(g) + 4FeCl_3(g)$ AND EQUILIBRIUM CONSTANTS

Temp. °K	Flow lit./ hour	$AlCl_3$ trans- ported g.	Fe_2O_3 reacted g.	$P_{AlOCl} \times 10^{-3}$ atm.	P_{FeCl_3} atm.	$P_{AlCl_3} \times 10^{-2}$ atm.	K_p	$-\log K_p$
1233	4.0	1.2413	0.0572	3.2843	4.3790×10^{-3}	5.1430	3.6177×10^{-11}	10.4415
1261	4.0	1.4049	0.0724	4.1570	5.5427×10^{-3}	5.7474	1.0812×10^{-10}	9.9661
1295	3.8	1.2378	0.0750	4.5329	6.0439×10^{-3}	5.2173	3.2183×10^{-10}	9.4924
1327	3.8	1.3741	0.0895	5.4093	7.2124×10^{-3}	5.7288	6.9297×10^{-10}	9.1593
1365	4.0	1.3176	0.1002	5.7532	7.6709×10^{-3}	5.0817	1.9444×10^{-9}	8.7113
1390	3.9	1.2679	0.1092	6.4307	8.5743×10^{-3}	4.8898	5.1440×10^{-9}	8.2887
1413	3.7	1.3769	0.1303	8.0881	1.0784×10^{-2}	5.4759	1.4527×10^{-8}	7.8377
1441	3.8	1.5350	0.1589	9.6038	1.2805×10^{-2}	5.8067	3.6035×10^{-8}	7.4433

The experiments were carried out for 1 hour.

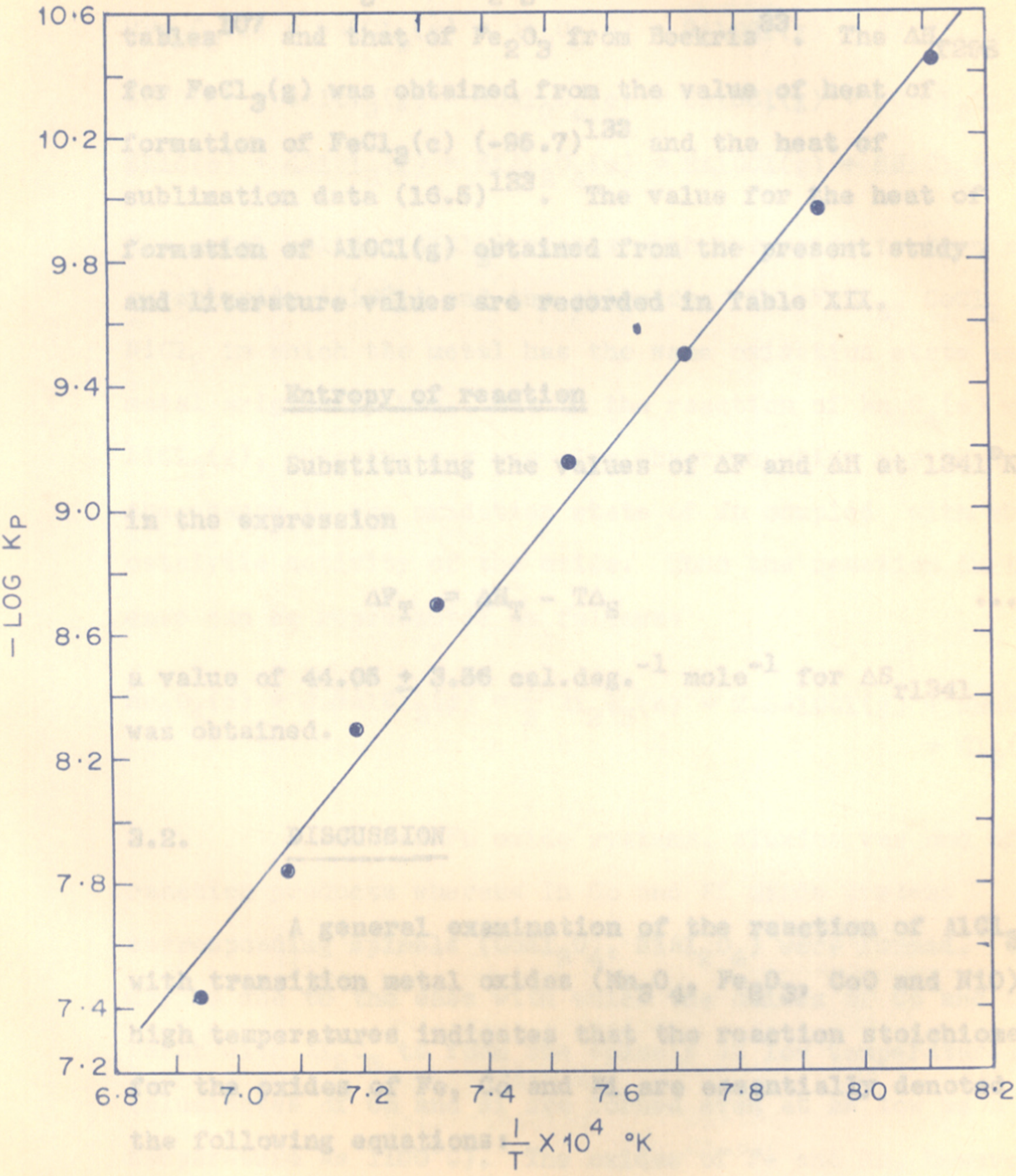


FIG. 10. PLOT OF LOG K_P VS $1/T \times 10^4$ FOR THE REACTION $2\,Fe_2O_3(c) + 5\,AlCl_3(g) = Al_2O_3(c) + 3\,AlOCl(g) + 4\,FeCl_3(g)$.

values for $AlCl_3(g)$, $Al_2O_3(c)$ were taken from JANAF tables[107] and that of Fe_2O_3 from Bockris[33]. The ΔH_{f298} for $FeCl_3(g)$ was obtained from the value of heat of formation of $FeCl_3(c)$ (-95.7)[133] and the heat of sublimation data (16.5)[133]. The value for the heat of formation of AlOCl(g) obtained from the present study and literature values are recorded in Table XIX.

Entropy of reaction

Substituting the values of ΔF and ΔH at 1341°K in the expression

$$\Delta F_T = \Delta H_T - T\Delta_S \qquad \ldots(52)$$

a value of 44.05 ± 3.56 $cal.deg.^{-1}$ $mole^{-1}$ for ΔS_{r1341} was obtained.

3.2. DISCUSSION

A general examination of the reaction of $AlCl_3(g)$ with transition metal oxides (Mn_3O_4, Fe_2O_3, CoO and NiO) at high temperatures indicates that the reaction stoichiometries for the oxides of Fe, Co and Ni are essentially denoted by the following equations:

$$2Fe_2O_3(c) + 5AlCl_3(g) = Al_2O_3(c) + 3AlOCl(g) + 4FeCl_3(g) \quad ..(101)$$

$$6CoO(c) + 4AlCl_3(g) = CoAl_2O_4(c) + 2AlOCl(g) + 5CoCl_2(g) \quad ..(96)$$

$$6NiO(c) + 4AlCl_3(g) = NiAl_2O_4(c) + 2AlOCl(g) + 5NiCl_2(g) \quad ..(106)$$

The metal halide ($AlCl_3$) reacts with the oxide to form an oxychloride ($AlOCl$) and the chlorides viz. $FeCl_3$, $CoCl_2$ or $NiCl_2$ in which the metal has the same oxidation state as the metal originally had. But in the reaction of $Mn_3O_4(c)$ with $AlCl_3(g)$, chlorine gas was also observed which may be due to the change in the oxidation state of Mn coupled with the catalytic activity of the oxide. Thus the reaction in this case can be represented as follows:

$$Mn_3O_4(c) + 3.5AlCl_3(g) = \frac{1}{2}\,Al_2O_3(c) + 2.5AlOCl(g) + 3MnCl_2(g) + Cl_2(g) \quad ..(86)$$

In Mn and Fe oxide systems, alumina was one of the reaction products whereas in Co and Ni oxide systems corresponding spinels ($CoAl_2O_4$, $NiAl_2O_4$) were formed. This may be due to the ease with which the oxides of Co and Ni react with Al_2O_3 to form the spinels at low temperatures (aluminates of Co and Ni are formed even at as low ~~as~~ a temperature as 1100°C). The oxides of Fe and Mn, however, form the aluminates at comparatively higher temperatures (about 1400°C).

The experimental log K_{ps} at different temperatures for the above four reactions are recorded in Table XVIII. From the plot of log K_p vs temp. (Fig.11) it can be said that the reaction of the halide ($AlCl_3$) with NiO and CoO is more favourable than that of Mn_3O_4 and Fe_2O_3 between 1000-1500°K, At lower temperatures (1000-1150°K) the reactivity of Fe_2O_3 is greater than that of Mn_3O_4. However, at temperatures beyohd 1150°K, the reaction of Mn_3O_4 with $AlCl_3$ is more favoured than that of Fe_2O_3. Thus an increasing trend of the reaction has been observed as one moves in the periodic table from Mn to Ni.

The values obtained for the heat of formation of AlOCl(g) in the present study together with the literature values are summarized in Table XIX.

Table XIX

Values for the heat of formation of AlOCl(g)

ΔH_{f298} AlOCl(g) Kcal.	Method	Reference	Sec.	Eq. No.
- 84.0 ± 5	Molecular effusion	124		
-83.6 ± 2.5	Transpiration	134		
-91.67 ± 2.35	Transpiration	Present work Chapter III	1	86
-83.14 ± 2.00	"	"	2	96
-80.41 ± 1.59	"	"	3	101

TABLE XVIII

CALCULATED LOG K_{ps} FOR VARIOUS REACTIONS AT DIFFERENT TEMPERATURES

Eqn. No.	Reaction	Temp. °K 1000	1100	1200	1300	1400	1500
86	$Mn_3O_4(c) + 3.5AlCl_3(g) = 1/2\ Al_2O_3(c) + 2.5AlOCl(g) + 3MnCl_2(g) + Cl_2(g)$	15.90	13.20	10.60	7.97	5.30	2.55
101	$2Fe_2O_3(c) + 5AlCl_3(g) = Al_2O_3(c) + 3AlOCl(g) + 4FeCl_3(g)$	13.75	12.30	10.90	9.50	8.00	~~x~~ 6.50
96	$6CoO(c) + 4AlCl_3(g) = CoAl_2O_4(c) + 2AlOCl(g) + 5CoCl_2(g)$	12.00	9.75	7.46	5.22	2.90	0.58
106	$6NiO(c) + 4AlCl_3(g) = NiAl_2O_4(c) + 2AlOCl(g) + 5NiCl_2(g)$	10.05	7.85	5.65	3.40	1.15	-

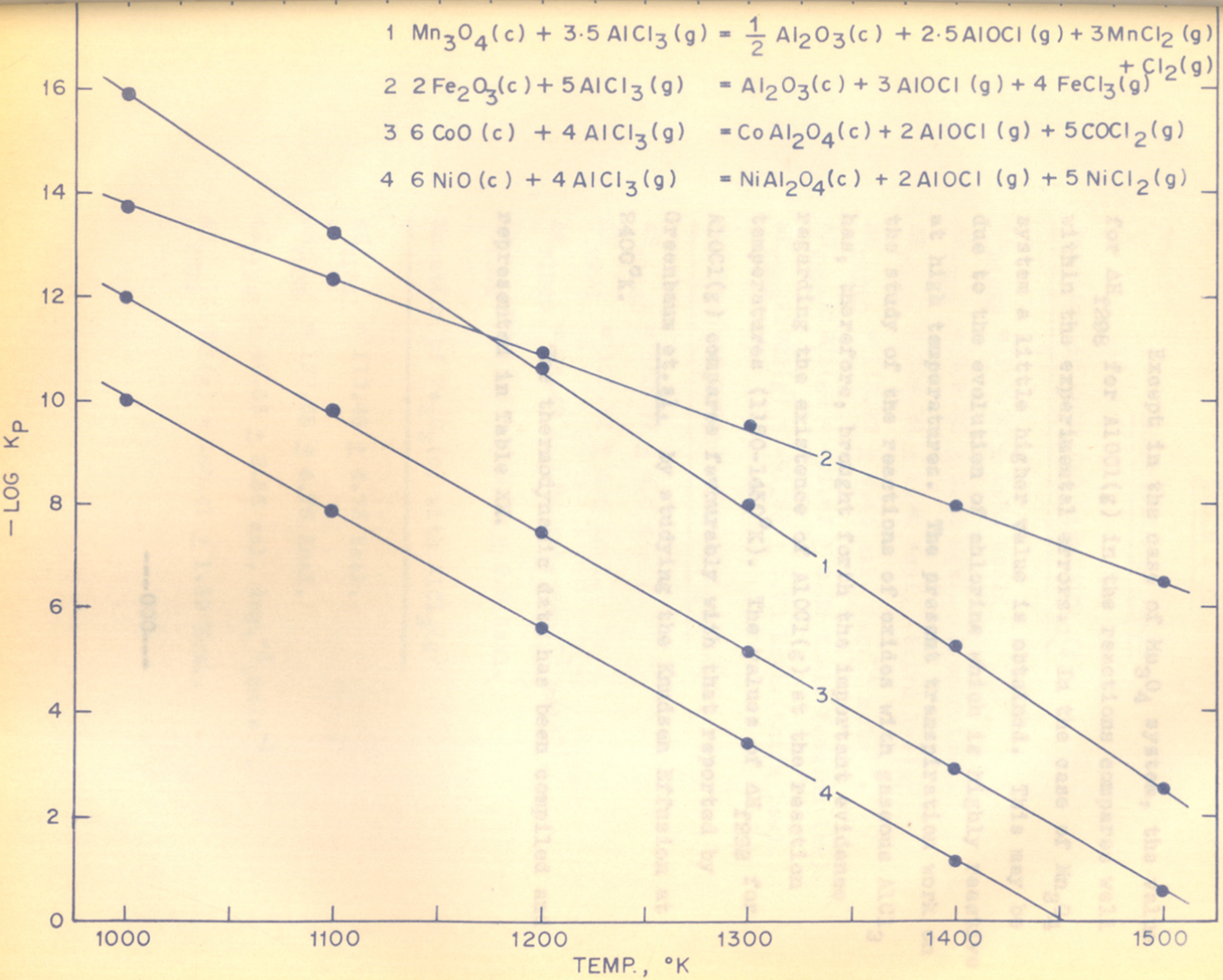


FIG. 11. PLOT OF LOG K_P VS TEMPERATURE FOR VARIOUS REACTIONS

Except in the case of Mn_3O_4 system, the value for ΔH_{f298} for AlOCl(g) in the reactions compares well within the experimental errors. In the case of Mn_3O_4 system a little higher value is obtained. This may be due to the evolution of chlorine which is highly reactive at high temperatures. The present transpiration work on the study of the reactions of oxides with gaseous $AlCl_3$ has, therefore, brought forth the important evidence regarding the existence of AlOCl(g) at the reaction temperatures (1150-1450°K). The value of ΔH_{f298} for AlOCl(g) compares favourably with that reported by Greenbaum et.al. by studying the Knudsen Effusion at 2400°K.

The thermodynamic data has been compiled and represented in Table XX.

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TABLE - XX

THERMODYNAMIC DATA

Reaction of $Mn_3O_4(c)$ with $AlCl_3(g)$

ΔH_{r1329} = 193.92 ± 5.88 Kcal.

ΔH_{r298} = 208.88 ± 5.88 Kcal. (second law).

ΔH_{r298} = 209.92 ± 1.96 Kcal. (third law).

ΔS_{r1329} = 113.72 ± 4.44 cal. deg.$^{-1}$ mole^{-1}.

ΔH_{f298} AlOCl(g) = -91.67 ± 2.35 Kcal. (second law).

ΔH_{f298} AlOCl(g) = -91.25 ± 0.78 Kcal.(third law).

Reaction of CoO(c) with $AlCl_3(g)$

ΔH_{r1240} = 153.97 ± 4.0 Kcal.

ΔH_{r298} = 172.12 ± 4.0 Kcal.

ΔS_{r1240} = 94.42 ± 3.24 cal. deg.$^{-1}$ mole^{-1}.

ΔH_{f298} AlOCl(g) = -83.14 ± 2.0 Kcal.

Reaction of $Fe_2O_3(c)$ with $AlCl_3(g)$

ΔH_{r1341} = 113.45 ± 4.76 Kcal.

ΔH_{r298} = 133.68 ± 4.76 Kcal.

ΔS_{r1341} = 44.05 ± 3.56 cal. deg.$^{-1}$ mole^{-1}.

ΔH_{f298} AlOCl(g) = -80.41 ± 1.59 Kcal.

SUMMARY

SUMMARY

Reactions involving metal-metal halides viz. Mn-$MnCl_2$ and Mn-$AlCl_3$ and the reaction of aluminium trichloride with transition metal oxides viz. Mn_3O_4, CoO and Fe_2O_3 were studied at high temperatures employing transpiration technique.

(1) Vapour pressure of $MnCl_2$

The vapour pressure of $MnCl_2$ has been determined between the temperatures 993 and 1218°K. The second law calculations yield for the heat of vaporization ΔH_{298} a value 52.42 ± 1.27 Kcal. which compares favourably with the third law value 54.52 ± 0.78 Kcal.

(2) Equilibrium reaction
$Mn(c) + MnCl_2(g) \rightleftharpoons 2MnCl(g)$

The reaction has been studied between 1243 and 1413°K. Over the temperature range the ΔH_r is found to be 57.64 ± 1.64 Kcal. The corresponding third law value obtained is 66.35 ± 1.1 Kcal. These values give -1.53 ± 0.82 and 2.83 ± 0.54 Kcal./mole respectively for the heat of formation of manganese monochloride. The entropy of reaction at 1328°K is 22.83 ± 1.24 cal.deg.$^{-1}$mole^{-1}.

(3) Reaction of $AlCl_3(g)$ with $Mn(c)$ metal

The reaction has been carried out between 1221-1403°K. The products of the reaction and the weight loss measurements suggest the following reaction:

$$2Mn(c) + AlCl_3(g) = MnCl_2(g) + MnCl(g) + Al(l)$$

The reaction yields a third law heat, $\Delta H_{298} = 81.12 \pm 0.93$ Kcal./mole which compares favourably with the second law value of 77.39 ± 2.49 Kcal./mole. These values give for the heat of formation of MnCl -0.27 ± 0.68 Kcal./mole and -4.01 ± 2.49 Kcal./mole respectively which are in good agreement with those obtained earlier. The entropy of reaction at 1311°K is 39.05 ± 1.91 $cal.deg.^{-1}$ $mole^{-1}$.

(4) Reaction of $AlCl_3(g)$ with $Mn_3O_4(c)$

The reaction was investigated between 1213 and 1433°K. From the weight loss data and analysis of the products, the reaction could be represented by the following stoichiometry

$$Mn_3O_4(c) + 3.5AlCl_3(g) = \frac{1}{2}Al_2O_3(c) + 2.5AlOCl(g) + 3MnCl_2(g) + Cl_2(g)$$

The heat of reaction was found to be 208.88 ± 5.88 Kcal./mole which was in good agreement with the corresponding third law value 209.92 ± 1.96 Kcal./mole. These values yielded for the heat of formation of $AlOCl(g)$ -91.67 ± 2.35 Kcal./mole and -91.25 ± 0.78 Kcal./mole respectively. The ΔS_r at 1329°K was found to be 113.72 ± 4.44 cal.deg.$^{-1}$ mole^{-1}.

(5) Reaction of $AlCl_3(g)$ with $CoO(c)$

The reaction was studied between the temperatures 1124-1361°K. The experimental data suggests the following stoichiometry

$$6CoO(c) + 4AlCl_3(g) = CoAl_2O_4(c) + 5CoCl_2(g) + 2AlOCl(g)$$

As the heat content functions are not available for $CoAl_2O_4(c)$ the calculations were restricted to second law only. The second law heat yielded for the heat of reaction a value 172.12 ± 4.0 Kcal. A value -83.14 ± 2.0 Kcal. was obtained for the heat of formation of $AlOCl(g)$ at 298°K which compares well with that reported in literature (ΔH_{f298} = -84 ± 5 Kcal.). The entropy of reaction at 1240°K was 94.42 ± 3.24 cal.deg.$^{-1}$ mole^{-1}.

(6) Reaction of $AlCl_3(g)$ with $Fe_2O_3(c)$

The reaction was studied between 1233-1441°K. Analysis of the products and the weight loss data suggest the following stoichiometry:

$$2Fe_2O_3(c) + 5AlCl_3(g) = Al_2O_3(c) + 3AlOCl(g) + 4FeCl_3(g)$$

The second law calculations gave for the heat of reaction ΔH_{298} a value 133.68 ± 4.76 Kcal. From this value the heat of formation of $AlOCl(g)$ was calculated and found to be -80.41 ± 1.59 Kcal./mole which is in good agreement with the earlier as well as reported values. The entropy of reaction at 1341°K was 44.05 ± 3.56 cal.deg.$^{-1}$ mole^{-1}.

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Vapour Pressures of Manganese Chloride & Study of the Equilibrium Reaction $Mn(c)+MnCl_2(g) \rightleftharpoons 2MnCl(g)$ at High Temperatures*

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The vapour pressure of $MnCl_2$ has been determined between the temperatures 993° and 1218°K. employing a transpiration technique. The second law calculations yield for the heat of sublimation ΔH_{298} a value $52{\cdot}42 \pm 1{\cdot}27$ kcal., which compares favourably with the third law value $54{\cdot}52 \pm 0{\cdot}78$ kcal. The equilibrium reaction $Mn(c)+MnCl_2(g) \rightleftharpoons 2MnCl(g)$ has been investigated between 1243° and 1413°K., employing a flow method. Over the temperature range the (ΔH_r) is found to be $57{\cdot}74 \pm 1{\cdot}64$ kcal. and entropy of reaction ($\Delta S_{r_{1328}}$), $22{\cdot}83 \pm 1{\cdot}24$ cal. deg.$^{-1}$.

THE heat of formation of MnCl(g) has not been determined experimentally. Available literature values are only the estimates based on the dissociation energy of the MnCl(g) molecule. Herzeberg[1] reported the dissociation energy (D_0) of the manganese subhalide as 3·3 eV., whereas Gaydon[2] obtained a value of 3 ± 1 eV. Using the heat of sublimation of manganese 66·73 kcal. mole^{-1} (ref. 3) and the dissociation energy of chlorine 57·8 kcal. mole^{-1} (ref. 4), the values obtained for the heat of formation of MnCl(g) are +19·84 kcal. mole^{-1}, and +26·74 ± 23 kcal. mole^{-1} respectively.

Lee[5] observed no appreciable transport of manganese by manganese chloride below 1273°K. even at 0·1 mm. pressure. However, experimental details are not available. Employing the heat content functions[6] and entropies of the MnCl(g) listed by Kelley and King[7], the free energy functions for $MnCl_2$ and Mn given by Brewer *et al.*[8] and Stull and Sinke[9] respectively, and the heat of formation of $MnCl_2$ calculated from the dissociation energies, it is possible to find out the transport of Mn. Alternatively, if the transported manganese is determined experimentally, the heat of formation of MnCl(g) can be calculated.

To facilitate the study of transport of Mn by the equilibrium reaction

$$Mn(c)+MnCl_2(g) \rightleftharpoons 2MnCl(g) \qquad \ldots(1)$$

the vapour pressure data for $MnCl_2$ is a must and hence the vaporization of the dichloride was carried out. The vaporization behaviour of $MnCl_2$ was first reported by Maier[10]. Later Schäfer *et al.*[11] found the pressure of manganese chloride over the temperature range 999° and 1216°K. by transpiration technique. Recent mass spectrometric study of the transpiration metal(II) halides by Schoonmaker *et al.*[12] revealed that $MnCl_2$ vaporizes predominantly as a monomer and the dimerization is negligible. However, his vapour pressure data when extrapolated to the temperature studied by Schäfer and coworkers[11] deviated by an order of magnitude due to slight dimerization. Pressures of manganese chloride observed[11] are slightly higher than those of Schoonmaker *et al.*[12].

The experimental results of the following studies are included in this publication: (1) Vaporization of $MnCl_2$ at temperatures between 993° and 1218°K.; and (2) equilibrium reaction (1) at temperatures between 1243° and 1413°K.

Experimental Procedure

Manganese chloride ($MnCl_2 4H_2O$), BDH Analar grade, was dehydrated in a stream of dry HCl(g) at 200° for 2 hr. Manganese metal flakes of 99·995 per cent purity supplied by Koch-Light Laboratories Ltd, England, have been used. Argon was used as a carrier gas.

Purification of argon gas — It is necessary to purify argon as the impurities like oxygen, moisture and nitrogen will react with manganese forming various oxides and nitrides. The purification process used by Gross *et al.*[13] served well during the present work. In addition, sofnolite (soda lime containing a little manganic acid) was used to remove carbon dioxide. Freshly prepared manganous oxide[14], which can absorb oxygen up to less than 1 p.p.m., was employed.

Vaporization of $MnCl_2$ — A Kanthal wound tube furnace was constructed, which gave a constant temperature zone (±3°C.) of 15 cm. length at temperatures between 970° and 1300°K. A silica tube (length 70 cm.; int. diam. 2 cm.) was used as the reaction tube. To maintain a constant power supply, the Kanthal heating elements were connected to the 230 V. main source through a voltage stabilizer. The reaction tube is fused on either side to B-24 silica joints. Temperature was measured by means of a calibrated chromel-alumel thermocouple. A flowmeter was employed to measure the rate of flow of carrier gas.

The reaction tube was completely flushed with oxygen-free argon gas. After attaining the required constant temperature and raising the argon gas rate to a desired value, the boat containing anhydrous manganese chloride was introduced from the downstream end and the experiment started. The experimental run was carried out for a definite time after which the boat was pushed out of the hot zone and the heating stopped. The system was allowed to cool in an argon atmosphere and the boat with the manganese chloride was weighed. Loss in weight of the manganese chloride was also

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TABLE 1 — TRANSPIRATION DATA AND THE THIRD LAW HEATS FOR THE VAPORIZATION OF $MnCl_2(l) \rightleftharpoons MnCl_2(g)$

Temp. °K.	Rate of flow of argon gas litre/hr	$MnCl_2$ transported		$P_{mm.}$	$-RT \ln K_p$ kcal.	ΔH_{298} kcal.
		g.	Moles			
993	2·25	0·0289	$2{\cdot}3004 \times 10^{-4}$	1·63	12·130	53·74
998	2·16	0·0283	$2{\cdot}2488 \times 10^{-4}$	1·65	12·158	53·94
1023	2·28	0·0475	$3{\cdot}7785 \times 10^{-4}$	2·63	11·520	54·07
1053	2·22	0·0831	$6{\cdot}6074 \times 10^{-4}$	4·71	10·638	54·06
1088	2·22	0·1085	$8{\cdot}6218 \times 10^{-4}$	6·31	10·358	54·78
1123	2·22	0·1705	$1{\cdot}3548 \times 10^{-3}$	9·59	9·760	55·17
1148	2·28	0·2708	$2{\cdot}1518 \times 10^{-3}$	14·74	8·996	55·13
1173	2·25	0·4568	$3{\cdot}6303 \times 10^{-3}$	24·80	7·978	54·80
1188	2·28	0·4791	$3{\cdot}8071 \times 10^{-3}$	25·63	8·002	55·24
1218	2·16	1·1180	$8{\cdot}8844 \times 10^{-3}$	59·98	6·146	54·24
					Av.=	54·52 ±0·78

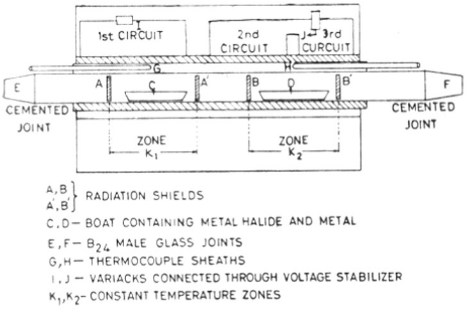

Fig. 1 — Diagram of a special tube furnace for studying equilibrium reaction (1)

checked by chemical analysis of the residual manganese chloride. The vaporization was carried out at different temperatures and the results are recorded in Table 1.

The values for the vapour pressures are in reasonable agreement with those reported by Schäfer and coworkers[11]. The vapour pressure data have been employed in the study of the equilibrium reaction (1).

Study of equilibrium reaction (1) — To study this reaction a special tube furnace (Fig. 1) wound with Kanthal-A heating element was constructed, which could give two different constant temperature zones K_1 and K_2, each 10 cm. in length and with a temperature variation of ±5°C. This was necessary to prevent the condensation of manganese chloride vapour in the middle of the reaction tube. A mullite refractory tube (length 100 cm.; int. diam. 1·5 cm.) was used as the reaction tube. B-24 pyrex joints were connected to either end of the tube with a high alumina refractory cement (Accoset-50) which helped to give cemented gas-tight joints. The two constant temperature zones were long enough to accommodate two boats C and D respectively. To maintain a constant power supply, the Kanthal heating elements were connected to a 230 V. main source through a voltage stabilizer. Temperatures were measured by means of calibrated chromel-alumel thermocouples G and H positioned over the central parts of the boats. The boat C containing manganese chloride was kept at about 1170°K. After attaining the constant temperature in the reaction zone, the boat D containing manganese metal was introduced from the downstream end. The experiment was started and allowed to run for a certain time. At the end of the run, the heating was stopped and the two boats were moved out of the hot zones. A series of such experiments was carried out at different temperatures and the amounts of Mn metal transported were calculated from the weight loss measurements.

Calculation of vapour pressure, equilibrium constant free energy and heat of reaction — In the transpiration method, it is necessary to determine the limits of the flow rates of the carrier gas saturated with the gaseous reaction products. This helps to know the extent to which the experimental results are being influenced by the diffusion transport. If an equilibrium between a gaseous 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 mixture[15].

In the present experiment, the transport of vapour is directly proportional to the loss in weight of metal manganese. The reaction (1) was studied at a temperature of 1333°K. by varying the flow rate of the carrier gas (containing $MnCl_2$) between 20 and 70 ml./min. When the data for weight loss were plotted against the flow rates in the above range, it increased linearly, thereby indicating that the flow gas was saturated with the gaseous reaction products. In a few preliminary experiments it was found that the weight of the alumina boat increased considerably (nearly 10 per cent). After each succeeding run, the increase in weight got reduced. However, this experimental discrepancy was minimized by weighing the metal flakes separately. Blank experiments carried out with manganese metal and by transporting $MnCl_2$ over the empty boat showed no perceptible increase in the weight of the boat. It was observed that the inner and outer surfaces of the alumina boat got covered with a thin layer of black material. The attack was found to be due to highly corrosive MnCl molecules.

The vapour pressure of manganese monochloride formed during the reaction (1) was calculated from Eq. (2):

$$\frac{P_a}{P_T} = \frac{P_a}{P_a+P_b+P_f} = \frac{n_a}{n_a+n_b+n_f} \qquad \ldots(2)$$

where P_a = the partial pressure of MnCl(g); P_T = total pressure; n_a = number of moles of MnCl(g) formed; n_b = number of moles of unreacted $MnCl_2$; and n_f = number of moles of argon collected during the run. In each run the amount of $MnCl_2$ passed and the amount of chemically transported manganese were determined by weight loss measurements.

The experimentally determined weight loss data of Mn(c) and $MnCl_2$(g) were converted to partial pressures of MnCl(g). The equilibrium constant for the reaction was calculated by substituting the pressures in expression (3).

$$K = \frac{P^2\mathrm{MnCl}}{P\mathrm{MnCl_2}} \qquad \ldots(3)$$

The free energy and heats of reaction at various temperatures were calculated employing Eq. (4) and (5):

$$\Delta F^{\circ} = -RT \ln K \qquad \ldots(4)$$

$$\frac{\Delta H^{\circ}_{298}}{T} = -R \ln K - \Sigma \frac{F^{\circ}_T - H^{\circ}_{298}}{T} \text{ (products)} + \Sigma \frac{F^{\circ}_T - H^{\circ}{}_{98}}{T} \text{ (reactants)} \qquad \ldots(5)$$

The free energy functions $\frac{F^{\circ}_T - H^{\circ}_{298}}{T}$ for the products and reactants were taken from Kelley[6,7].

Results and Discussion

$MnCl_2$ vaporization — In the treatment of the vapour pressure data for $MnCl_2$ system, the polymerization of the dihalide vapours is not taken into account as Schoonmaker *et al.*[12] have reported that monomer is the major vapour species in their mass spectrometric studies on the vaporization of $MnCl_2$. In view of this information the vapour pressures for $MnCl_2$ recorded in Table 1 were calculated from the assumption that the manganese chloride vaporized as a monomer

$$MnCl_2(1) \rightleftharpoons MnCl_2(g) \qquad \ldots(6)$$

Third law heats calculated are given in Table 1.

Employing the well-known Vant Hoff's equation

$$(d \ln K)\ d\ 1/T = -\Delta H/R \qquad \ldots(7)$$

the heat of vaporization ΔH_v has been determined from the plot of the logarithm of the equilibrium constant versus the reciprocal of the absolute temperature (Fig. 2). The points representing the experimental values show a good fit with the straight line obtained by least squares method. The plot of this data gives an equation:

$$\log P = \frac{-7{,}729 \pm 277{\cdot}48}{T} + 5{\cdot}1079 \pm 0{\cdot}25 \qquad \ldots(8)$$

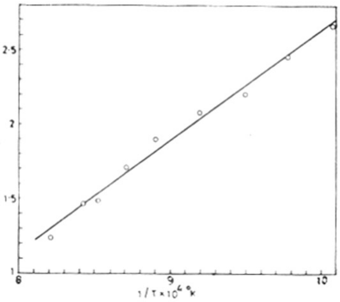

Fig. 2 — Plot of log P versus $1/T$ for the vaporization of $MnCl_2(c) = MnCl_2(g)$

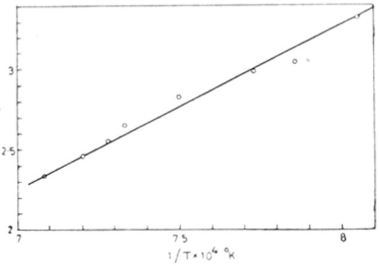

Fig. 3 — Plot of log K_p versus $1/T$ of the reaction (1)

The second law heat obtained from the above equation is $\Delta H^{\circ}_{1106} = 35{\cdot}37 \pm 1{\cdot}27$ kcal. When corrected to 298°K. assuming $\Delta C_p = -10$ cal. deg. mole[16] for the vaporization process, the heat of vaporization ΔH_{298} becomes $43{\cdot}45 \pm 1{\cdot}27$ kcal. Using the heat of fusion 8·97 kcal., as given by Brewer *et al.*[8], the heat of vaporization becomes $52{\cdot}42 \pm 1{\cdot}27$ kcal. This is in fair agreement with the third law value $54{\cdot}52 \pm 0{\cdot}78$ kcal. The difference may be due to the temperature dependent errors which contribute considerably to the second law or may be due to the errors in ΔC_p values.

The second law entropy of vaporization $\Delta S_{1106} = 23{\cdot}37 \pm 1{\cdot}16$ cal. $deg.^{-1}$ does not differ very much from that of the third law value 25·27 cal. $deg.^{-1}$.

Reaction $Mn(c)+MnCl_2(g) \rightleftharpoons 2MnCl(g)$ — The experimental data for this reaction have been summarized in Table 2. Employing Vant Hoff's equation, the heat of reaction ΔH_r has been determined from the plot of log K versus $1/T$°K. (Fig. 3). The slope of the line obtained by the method of least squares gave the heat of reaction $\Delta H_r = 47{\cdot}34 \pm 1{\cdot}64$ kcal. This value of ΔH_r represents the mean over the temperature range studied. The value for ΔH_{298} could be calculated from the knowledge of ΔH_{1328} and the functions cited by Kelley[6,7]. As the heat content functions are not available, a ΔC_p value of −10 cal. (ref. 16) has been assumed for converting $MnCl_2$(l) to $MnCl_2$(g). The value of $\Delta(H_{1328}-H_{298})$ for the reaction (1), therefore, becomes −10·4 kcal. The value of ΔH_r at 298°K. is thus $57{\cdot}74 \pm 1{\cdot}64$ kcal. The corresponding third law value is $66{\cdot}35 \pm 1{\cdot}1$ kcal.

TABLE 2 — TRANSPIRATION DATA FOR REACTION (1)

Temp. °K.	Rate of flow of argon gas litre/hr	$MnCl_2$ passed g.	Loss in Mn metal mg.	P(MnCl) atm.	$P(MnCl_2)$ atm. $\times 10^{-2}$	K_p	$-RT \ln K_p$ kcal.	ΔH_{298} kcal.
1243	2·16	0·3999	9·10	$3{\cdot}788\times10^{-3}$	3·444	$4{\cdot}1657\times10^{-4}$	19·226	65·79
1273	2·16	1·1033	22·22	$9{\cdot}249\times10^{-3}$	9·562	$8{\cdot}9456\times10^{-4}$	17·757	65·27
1293	2·22	0·7108	19·20	$7{\cdot}776\times10^{-3}$	5·895	$1{\cdot}0256\times10^{-3}$	17·684	65·82
1333	2·25	0·8540	25·25	$1{\cdot}009\times10^{-2}$	6·944	$1{\cdot}4658\times10^{-3}$	17·285	66·71
1363	2·22	0·5034	23·40	$9{\cdot}477\times10^{-3}$	3·978	$2{\cdot}2574\times10^{-3}$	16·505	66·89
1373	2·40	1·1050	40·95	$1{\cdot}534\times10^{-2}$	8·269	$2{\cdot}8458\times10^{-3}$	15·994	66·70
1388	2·58	1·1282	46·85	$1{\cdot}633\times10^{-2}$	7·766	$3{\cdot}4323\times10^{-3}$	15·652	6σ83
1413	2·40	0·8402	46·95	$1{\cdot}759\times10^{-2}$	5·991	$5{\cdot}1631\times10^{-3}$	14·788	66·76
							Av.=	66·35 ±1·1

The deviation from the third law heat may be due to the temperature dependent errors in the second law coupled with the side reaction of the highly unstable and corrosive MnCl gas with the container material. Hence, the second law heat of reaction permits the calculation of the heat of formation of MnCl(g) from Eq. (9)

$$\Delta H_{f298}\text{MnCl(g)} = \tfrac{1}{2}[\Delta H_{f298} + \Delta H_{f298}\ \text{MnCl}_2\text{(g)} + \Delta H_{f298}\ \text{Mn(c)}] \quad \ldots(9)$$

as $-1{\cdot}48 \pm 0{\cdot}82$ kcal. and the corresponding third law value gives $2{\cdot}83 \pm 0{\cdot}27$ kcal. The $\Delta H_{f298(g)}$ ($-60{\cdot}7$) for $MnCl_2$(g) was taken from Brewer *et al.*[8]. The entropy of the reaction ΔS_{r1328} was obtained from the intercept of the plot in Fig. 3 which led to a value of $22{\cdot}83 \pm 1{\cdot}24$ cal. deg.$^{-1}$. The corresponding third law value calculated by substituting the ΔH value in Eq. (10)

$$\Delta F_r = \Delta H_r - T\Delta S_r \quad \ldots(10)$$

was 29·31 cal. deg.$^{-1}$.

Thermodynamic properties — The values of various thermodynamic parameters can be summarized as follows:

For $MnCl_2$ vaporization

	Second law	Third law
ΔH_{298}	$52{\cdot}42 \pm 1{\cdot}27$ kcal.	$54{\cdot}52 \pm 0{\cdot}78$ kcal.
ΔS_{1106}	$23{\cdot}37 \pm 1{\cdot}16$ cal. deg.$^{-1}$	25·27 cal.

For reaction (1)

	Second law	Third law
ΔHf_{298} MnCl	$-1{\cdot}48 \pm 0{\cdot}82$ kcal.	$2{\cdot}83 \pm 0{\cdot}27$ kcal.
ΔS_{r1328}	$22{\cdot}83 \pm 1{\cdot}24$ cal. deg.$^{-1}$	29·31 cal.
ΔH_r	$57{\cdot}74 \pm 1{\cdot}64$ kcal.	$66{\cdot}35 \pm 1{\cdot}1$ kcal.

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