

Study of the Reaction $\text{Mn}(c) + \text{AlCl}(g) = \text{MnCl}(g) + \text{Al}(l)^*$

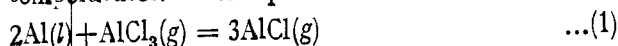
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The reaction of $\text{AlCl}(g)$ with $\text{Mn}(c)$ has been studied in temperature range 1375° to 1511°K. The heat of reaction ($\Delta H_r = 14.2 \text{ kcal mole}^{-1}$) has been obtained at the mean temperature of 1443°K. The experimental data are used to obtain the heat of formation of $\text{MnCl}(g)$ at 298°K by second law and third law methods. The second law method gave a value of $\Delta H_f^{298} = 1.2 \pm 1.3 \text{ kcal mole}^{-1}$ and that given by third law method is $\Delta H_f^{298} = -1.1 \pm 0.1$. Due to the highly corrosive nature of gaseous MnCl and AlCl , the system gets complicated and hence may be the contributing factor to the values of heats of formation for the manganese monohalide.

LEE¹ has reported a number of reactions by passing dissimilar anhydrous gaseous chlorides over different metals and alloys at elevated temperatures. The equilibrium reaction



has been extensively studied²⁻⁷ and the highly reactive nature of gaseous AlCl molecule has been studied by Rao and Dadape⁸. Manganese because of its multivalent nature was chosen for the study. The studies of band spectra by a number of workers⁹⁻¹² revealed the existence of gaseous monochloride. Available literature values are only the estimates based on the dissociation energy of $\text{MnCl}(g)$ molecule. Herzberg¹³ reported the dissociation energy (D_0) as 3.3 eV, whereas Gaydon¹⁴ obtained a value of 3 ± 1 eV. Bulewicz¹⁵ obtained from flame photometry ΔH_f of $\text{MnCl}(g)$ as +10.37 kcal, whereas a value of 10.1 kcal has also been reported¹⁶. Dadape and Murthy¹⁷ obtained by transpiration method as -1.48 ± 0.82 kcal by second law and 2.83 ± 0.27 kcal by third law method. In view of these discrepancies the equilibrium study of the reaction of $\text{AlCl}(g)$ and $\text{Mn}(c)$ at high temperatures has been undertaken employing transpiration technique.

Materials and Methods

Manganese metal flakes of 99.99% purity (Koch-Light) were used. Aluminium wire of 99.98% purity (BDH, AR) was degreased, melted in an argon atmosphere to expel the dissolved gases and the resulting ingot was cut into chips and used. AlCl_3 of 99.9% purity (E. Merck) was resublimed in an inert atmosphere before use. The resublimed product contained 0.04% of FeCl_3 and 0.2% alumina. The anhydrous sample was prepared in sealed glass tubes. Argon, used as a carrier gas, was purified by the method described earlier⁷.

Apparatus and procedure — A special tube furnace (Fig. 1) wound with platinum heating element was constructed which gave two different constant

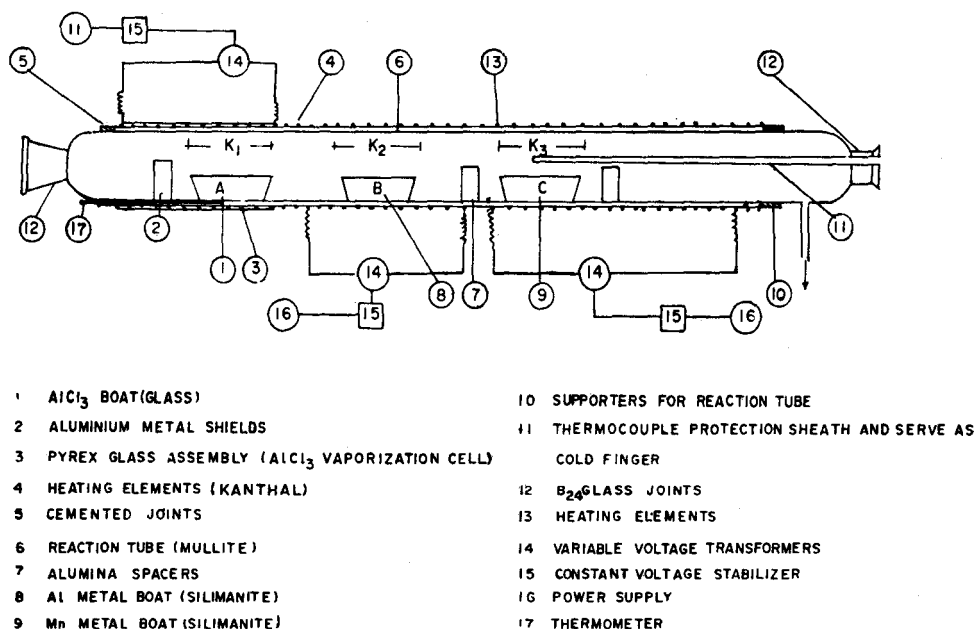
temperature zones, K_2 and K_3 each nearly 8-10 cm in length and with a temperature variation of $\pm 8^\circ$. A Kanthal ribbon was wound on one side of the tube to give a constant temperature zone (in which AlCl_3 vaporized) of about 8 cm with temperature variation of $\pm 3^\circ$. The constant temperature zones were long enough to accommodate boats (A, B and C) of 6 cm length and about 1.5 cm width. The insulation around the heating elements consisted of light refractory bricks. A mullite refractory tube (length 100 cm, internal diam. 2.0 cm) was used as the reaction tube.

After attaining the required temperatures in the three zones, the glass boat containing AlCl_3 , which was weighed previously, was positioned in its vaporization zone K_1 and the joint was immediately closed. The momentary exposure of AlCl_3 to the atmosphere in this operation was unavoidable. However, it had negligible effect on the experimental results. The boat containing aluminium metal was introduced from the downstream end in the zone K_2 . The argon rate was regulated to the desired value so that the percentage of $\text{AlCl}(g)$ produced was more than 85. The actual experiment was started by pushing the boat (C) containing manganese metal in the zone K_3 . After running for a definite time (1 hr) the reaction tube was moved in such a way that the boat containing AlCl_3 attained room temperature quickly thereby arresting the reaction, and the heating was stopped. Subsequently other two boats were pushed out of the hot zones. The system was allowed to cool in argon atmosphere. The AlCl_3 boat was pushed into the glass capsule containing dry argon. The transport of AlCl_3 was found by weight loss measurements and the extent of reaction was found out by weighing the boats containing Al metal and Mn metal. Unreacted Mn remaining in the boat was subjected to chemical analysis.

Temperatures were measured by means of calibrated Pt-Pt/Rh-10% thermocouple. A mercury thermometer was used to measure temperatures of the AlCl_3 vaporizer. A calibrated flow meter was employed to measure the flow of argon. A mullite sheath was introduced from the downstream end

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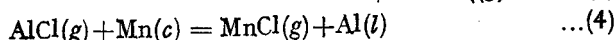
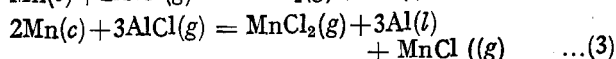
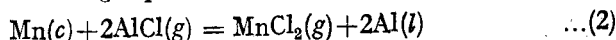
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 Fig. 1 — FURNACE FOR THE STUDY OF REACTION $\text{AlCl}_3(g) + \text{Mn}(c) = \text{MnCl}(g) + \text{Al}(l)$

which acted as a cold finger on which the gaseous reaction products were condensed.

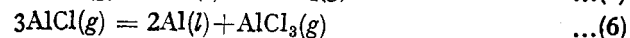
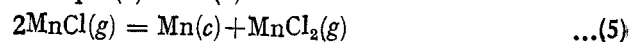
The attainment of equilibrium is an important criteria in the transpiration method. Keeping the temperature of the reaction constant, transpiration runs were carried out using argon as the carrier gas at flow rates 2.4-3.6 litres/hr. The previous study of the equilibrium reaction⁷ showed that the effects of self-diffusion and thermal-diffusion were negligible at these flow rates.

Analysis and identification of the products — The residue in the boat showed the presence of Al metal as revealed by X-ray and chemical analysis. However, the formation of Mn-Al alloy has not been ruled out. In the Al-Mn phase diagram at the Mn-rich end, the relevant curve gives the solubility of Al in manganese. Mn was determined gravimetrically (phosphate precipitation) and volumetrically (oxidation by sodium bismuthate). From the quantity of Al found in the reaction boat (C) the stoichiometry of the chemical reaction was arrived at. The probable reaction between $\text{AlCl}(g)$ and $\text{Mn}(c)$ may be understood by considering the following equations:



$\text{Mn}(c)$, MnCl_2 and Al metal are observed on the colder part of the tube and also on the cold finger. The Mn deposit proves that $\text{MnCl}(g)$ was present in the gaseous mixture. Thus reaction (2) which does not include $\text{MnCl}(g)$ can be neglected. The quantitative analysis of Al metal in the boat showed that one mole of Mn metal reacted to give one mole of Al metal. Hence reaction (3) can also be neglected. Therefore the reaction represented by Eq. (4) is the only possible reaction.

The residue in the boat containing unreacted manganese metal and small shining particles of aluminium was finely ground. X-ray and chemical analysis of the sample revealed the presence of Mn and Al. The gaseous products of the reaction carried by the carrier argon gas were condensed on the cold finger. The cold finger with the condensate was initially heated at 150° under reduced pressure to drive off AlCl_3 and then the temperature raised to about 800°, when all the MnCl_2 sublimed off leaving behind a black mass. Chemical and X-ray analysis of the mass showed it to be a mixture of Mn and Al. These metals may be produced due to the disproportionation of gaseous MnCl and AlCl according to Eqs. (5) and (6).



It may be mentioned here that Mn and Al have negligible vapour pressures at these temperatures.

The boat and the reaction tubes were attacked during the reaction. The boat got passivated after a few experiments and the reaction mullite tube could withstand $\text{MnCl}(g)$ only for 3-4 runs.

Treatment of the data — The vapour pressures of $\text{MnCl}(g)$ and $\text{AlCl}(g)$ were calculated from the experimentally determined weight loss of Mn, Al and AlCl_3 using the equation:

$$\frac{P_a}{P_t} = \frac{P_a}{P_a + P_b + P_c + P_d} = \frac{n_a}{n_a + n_b + n_c + n_d} \quad \dots(7)$$

where P_a is partial pressure of $\text{MnCl}(g)$; P_t is total pressure and n_a , n_b , n_c and n_d are the number of moles of Mn metal, unreacted $\text{AlCl}(g)$, unreacted $\text{AlCl}_3(g)$ and argon gas passed during the run respectively. They are calculated as follows:

$$n_b = (n\text{AlCl} - n\text{Mn}) \quad \dots(8a)$$

$$n_c = (n\text{AlCl}_3 - 1/2 n\text{Al}) \quad \dots(8b)$$

$$n_d = (V^\circ/22.4) \quad \dots(8c)$$

TABLE 1 — THERMODYNAMIC PROPERTIES OF THE REACTION $Mn(c) + AlCl_3(g) = MnCl(g) + Al(l)$

(Duration of experiment, 1 hr; flow of argon gas between 2.44 and 3.54 litres/hr; $AlCl_3$ transported, 3.35 to 4.5 g depending on flow rate and temperature; Al metal transported, 1.24 to 1.47 g depending on the amount of $AlCl_3$ gas)

No.	Temp. °K	Pressure ($\times 10$) of unreacted $AlCl_3(g)$ (atm)	Mn metal transported (mg)	Pressure of $MnCl(g)$ $\times 10^2$ (atm)	$K_p \times 10$	$-RT \ln K$ (kcal)	$T\Delta f_{ef}$ (kcal)	ΔH_{r298} (kcal)	ΔH_{f298} of $MnCl$ (kcal mole ⁻¹)
1	1375	2.97	473	4.25	1.4	5.31	7.24	12.6	-1.1
2	1396	2.98	503	4.52	1.5	5.24	7.38	12.8	-1.0
3	1419	3.21	611	5.47	1.7	4.99	7.47	12.5	-1.1
4	1442	2.75	655	5.00	1.8	4.88	7.54	12.5	-1.1
5	1489	3.43	780	7.19	2.1	4.63	7.83	12.5	-1.1
6	1511	3.40	822	7.78	2.3	4.43	7.94	12.4	-1.2

Av. -1.1 ± 0.1

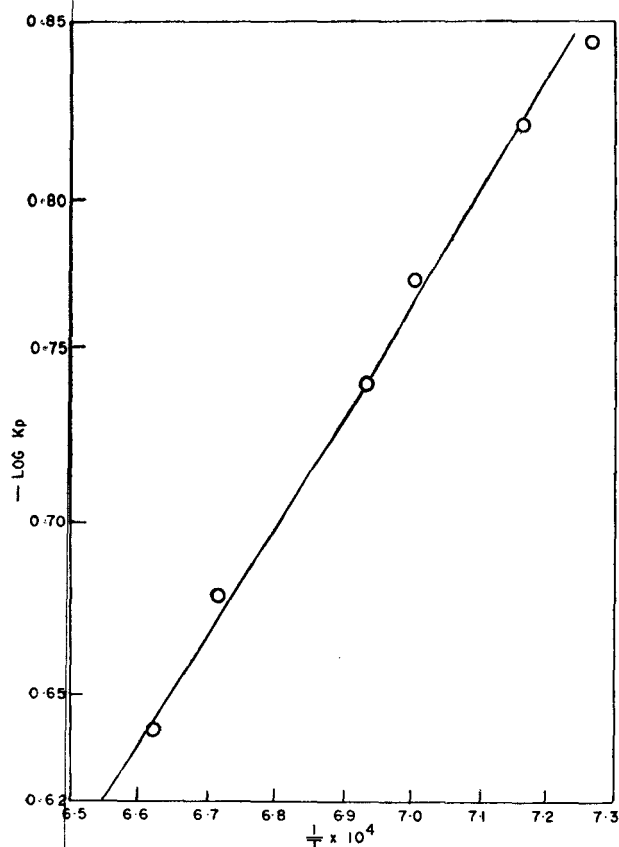


Fig. 2 — Plot of $-\log K_p$ versus $1/T$

Similarly, partial pressure of unreacted $AlCl_3(g)$ was given by

$$\frac{P_b}{P_t} = \frac{n_b}{n_a + n_b + n_c + n_d} \quad \dots(9)$$

The equilibrium constant for reaction (4) was calculated by substituting pressures in the expression:

$$K_p = \frac{P_{MnCl(g)}}{P_{AlCl_3(g)}} \quad \dots(10)$$

The free energy of the reaction was calculated at various temperatures employing the equation

$$\Delta G^\circ = -RT \ln K_p \quad \dots(11)$$

The transpiration data and calculated equilibrium constants, free energy and third law heats obtained from f_{efs} are recorded in Table 1.

Results and Discussion

From the plot of $\log K_p$ vs $1/T$ (Fig. 2) the value for the second law heat obtained was 14.2 ± 0.5 kcal. This value represents the mean over the temperatures studied. The value for ΔH_{r298} could be calculated from the knowledge of C_p values. This C_p values for $Mn(c)$ and $Al(l)$ metals were taken from Stull and Sinke²⁰. C_p values for $AlCl_3(g)$ and $MnCl(g)$ were from Kelley²¹. By applying Kirchoff's law ΔH_{r298} for the reaction was found to be 14.4 ± 0.5 kcal. The corresponding third law heat was 12.5 ± 0.3 kcal mole⁻¹. The reaction between $AlCl_3(g)$ and $Mn(c)$ was negligible compared to that between $AlCl_3(g)$ and $Mn(l)$. It may be stated here that dimer is not an important species at these temperatures. The solubility curves^{18,19} of Al in both α -Mn and β -Mn (in the Mn-rich region) are nearly parallel to the temperature axis and hence only negligible heat effects (1 to 2 kcal/g atom of Al) are probably involved. The deviation may be due to temperature-dependent errors coupled with side reactions and corrosive nature of $MnCl$ gas.

Heat of formation of $MnCl(g)$ — The second law heat of reaction permits the calculation of the heat of formation of $MnCl(g)$ according to Eq. (12).

$$\Delta H_{f298} MnCl(g) = \Delta H_{r298} = \Delta H_{f298} Al(l) + \Delta H_{f298} AlCl_3(g) \quad \dots(12)$$

The heat of formation of $MnCl(g)$ thus calculated yielded a value 1.2 ± 1.3 kcal mole⁻¹. The values for the heat of formation of $AlCl_3(g)$ ²² and $Al(l)$ ²³ were taken from "JANAF" tables. These values are in good agreement with that reported by Murthy and Dadape¹⁷ earlier.

Entropy of the reaction was calculated from least squares constant and was found to be 6.4 ± 0.4 e.u.

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