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Study of the Reaction Mn(c) + AlCl(g) = MnCl(g) + Al(l)*

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The reaction of AlCl(g) with Mn(c) has been studied in temperature range 1375° to 1511°K. The heat of reaction (ΔH₉₈ = 142 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 MnCl(g) at 298°K by second law and third law methods. The second law method gave a value of ΔH₉₈ = 12 ± 1 kcal mole⁻¹ and that given by third law method is ΔH₉₈ = -11 ± 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.

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. AlCl₃ of 99.9% purity (E. Merck) was sublimed in an inert atmosphere before use. The sublimed product contained 0.04% of FeCl₃ 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 earlier.

Apparatus and procedure — A special tube furnace (Fig. 1) wound with platinum heating element was constructed which gave two different constant temperature zones, K₁ and K₂ each nearly 8-10 cm in length and with a temperature variation of ± 3°. A Kanthal ribbon was wound on one side of the tube to give a constant temperature zone (in which AlCl₃ vaporized) of about 8 cm with temperature variation of ± 3°. 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 AlCl₃, which was weighed previously, was positioned in its vaporization zone K₁ and the joint was immediately closed. The momentary exposure of AlCl₃ 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 K₂. The argon rate was regulated to the desired value so that the percentage of AlCl₃ produced was more than 85%. The actual experiment was started by pushing the boat (C) containing manganese metal in the zone K₃. After running for a definite time (1 hr) the reaction tube was moved in such a way that the boat containing AlCl₃ 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 AlCl₃ boat was pushed into the glass capsule containing dry argon. The transport of AlCl₃ 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 AlCl₃ vaporizer. A calibrated flow meter was employed to measure the flow of argon. A mullite sheath was introduced from the downstream end...
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 2-4-5-6 litres/hr. The previous study of the equilibrium reaction 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 AlCl(g) and Mn(c) may be understood by considering the following equations:

\[
\text{Mn(c)} + 2\text{AlCl(g)} = \text{MnCl}_2(g) + 2\text{Al(l)} \quad \ldots (2)
\]

\[
2\text{Mn(c)} + 3\text{AlCl(g)} = 2\text{MnCl}_2(g) + 3\text{Al(l)} \quad \ldots (3)
\]

\[
\text{AlCl(g)} + \text{Mn(c)} = \text{MnCl(g)} + \text{Al(l)} \quad \ldots (4)
\]

Mn(c), MnCl and Al metal are observed on the colder part of the tube and also on the cold finger. The Mn deposit proves that MnCl(g) was present in the gaseous mixture. Thus reaction (2) which does not include 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. These metals may be produced due to the disproportionation of gaseous MnCl and AlCl according to Eqs. (5) and (6).

\[
2\text{MnCl(g)} = \text{Mn(c)} + \text{MnCl}_2(g) \quad \ldots (5)
\]

\[
3\text{AlCl(g)} = 2\text{Al(l)} + \text{AlCl}_3(g) \quad \ldots (6)
\]

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

**Treatment of data** — The vapour pressures of MnCl(g) and AlCl(g) were calculated from the experimentally determined weight loss of Mn, Al and AlCl by using the equation:

\[
P_{\text{MnCl}} = \frac{P_{\text{Mn}}}{P_{\text{Al}} + P_{\text{AlCl}}} = \frac{n_a}{n_a + n_b + n_c + n_d}
\]

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

\[n_a = (n\text{Mn})\]
\[n_b = (n\text{AlCl} - 1/2 n\text{Al})\]

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\[n_a = (n\text{Mn})\]
\[n_b = (n\text{AlCl} - 1/2 n\text{Al})\]
\[n_c = (n\text{AlCl})\]
\[n_d = (n\text{Al})\]

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\[n_a = (n\text{Mn})\]
\[n_b = (n\text{AlCl} - 1/2 n\text{Al})\]
\[n_c = (n\text{AlCl})\]
\[n_d = (n\text{Al})\]

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The transpiration data and calculated equilibrium constants, free energy and third law heats obtained from fes 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 $14.2 \pm 0.5$ kcal. This value represents the mean over the temperatures studied. The value for $\Delta H_{298}^\circ$ could be calculated from the knowledge of $C_p$ values. This $C_p$ values for Mn(g) and Al(l) metals were taken from Stull and Sinke. $C_p$ values for AlCl(g) and MnCl(g) were from Kelley. By applying Kirchhoff's law $\Delta H_{298}^\circ$ for the reaction was found to be $14.4 \pm 0.5$ kcal. The corresponding third law heat was $12.5 \pm 0.3$ kcal mole$^{-1}$.

The reaction between AlCl$_3$(g) and Mn(c) was negligible compared to that between AlCl(g) and Mn(c). It may be stated here that dimer is not an important species at these temperatures. The solubility curves of Al in both $\alpha$-Mn and $\beta$-Mn (in the Mn-rich region) are nearly parallel to the temperature axis and hence only negligible heat effects (1 to 2 kcal/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.

The 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).

$$\Delta H_{298}^\circ \text{MnCl}(g) = \Delta H_{298}^\circ \text{Al}(l) + \Delta H_{298}^\circ \text{AlCl}(g) \quad \text{(12)}$$

The heat of formation of MnCl(g) thus calculated yielded a value $1.2 \pm 1.3$ kcal mole$^{-1}$. The values for the heat of formation of AlCl(g)$^{23}$ and Al(l)$^{23}$ were taken from "JANAF" tables. These values are in good agreement with that reported by Murthy and Dadape$^{11}$ earlier.

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

### Table 1 — Thermodynamic Properties of the Reaction Mn(c) + AlCl(g) = MnCl(g) + Al(l)

(Reaction conditions: 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 gas)

<table>
<thead>
<tr>
<th>No.</th>
<th>Temp. (°K)</th>
<th>Pressure (×10$^2$ atm)</th>
<th>Mn metal transported (mg)</th>
<th>Pressure of MnCl(g) (atm)</th>
<th>$K_p \times 10^{-10}$</th>
<th>$-RT \ln K_p$ (kcal)</th>
<th>$\Delta H_{298}^\circ$ (kcal)</th>
<th>$\Delta H_{298}^\circ$ of MnCl (kcal mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1375</td>
<td>2.97</td>
<td>473</td>
<td>4.25</td>
<td>1.4</td>
<td>5.31</td>
<td>7.24</td>
<td>12.6</td>
</tr>
<tr>
<td>2</td>
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<td>2.98</td>
<td>503</td>
<td>4.52</td>
<td>1.5</td>
<td>5.24</td>
<td>7.38</td>
<td>12.8</td>
</tr>
<tr>
<td>3</td>
<td>1419</td>
<td>3.21</td>
<td>611</td>
<td>5.47</td>
<td>1.7</td>
<td>4.99</td>
<td>7.47</td>
<td>12.5</td>
</tr>
<tr>
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<td>2.75</td>
<td>655</td>
<td>5.00</td>
<td>1.8</td>
<td>4.88</td>
<td>7.54</td>
<td>12.5</td>
</tr>
<tr>
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<td>1489</td>
<td>3.43</td>
<td>780</td>
<td>7.19</td>
<td>2.1</td>
<td>4.63</td>
<td>7.83</td>
<td>12.5</td>
</tr>
<tr>
<td>6</td>
<td>1511</td>
<td>3.40</td>
<td>822</td>
<td>7.78</td>
<td>2.3</td>
<td>4.43</td>
<td>7.94</td>
<td>12.4</td>
</tr>
</tbody>
</table>

Av. $-1.1 \pm 0.1$
KULKARNI & DADAPE: REACTION OF Mn METAL WITH GASEOUS AlCl

16. Selected values of chemical thermodynamic properties, NBS technical notes No. 270-4 Series (US Department of Commerce), May 1969, 48.