CHAPTER III

VAPOUR PRESSURE OF CADMIUM METAL AND THE STUDY OF THE
REACTION $\text{Cd}(g) + \text{CdCl}_2(s) \rightarrow 2\text{CdCl}(g)$ AT HIGH TEMPERATURES.
VAPOUR PRESSURE OF CADMIUM METAL AND THE STUDY OF THE REACTION

\[ \text{Cd}_2(c) + \text{CdCl}_2(c) \rightleftharpoons 2\text{CdCl}(g) \] AT HIGH TEMPERATURES.

3.1 Introduction

Though the existence of cadmium monochloride has been reported by many investigators, the heat of formation of gaseous \text{CdCl} has not been determined experimentally.

In 1929, Wieland\(^96\) reported the presence of cadmium monochloride (\text{CdCl}) while studying the spectra in the region 7000°A-2000°A. In 1938, Cornell\(^97\) observed some additional bands while studying the U.V. band spectra of mercury, cadmium and zinc chlorides, which he attributed to \text{CdCl} in the region 3200°A-2000°A. Powell\(^98\) also reported the presence of \text{CdCl} in the U.V. region.

The available literature values are only estimates based on the dissociation energy of the gaseous \text{CdCl} molecule. Herzberg\(^99\) reported the dissociation energy of \text{CdCl}(g) as 2.8 e.v. whereas Gaydon\(^100\) obtained a value of 2.1 ± 0.03 e.v.

Bruner\(^101,102\) and Corbett studied the gas phase absorption spectra of the system \text{Cd}-\text{CdCl}_2 and its components at temperatures 545°-980°C. They observed that the mixture displayed new bands due to the presence of monochloride, the reaction being

\[ \text{Cd}(g) + \text{CdCl}_2(g) = 2\text{CdCl}(g) \] (42)
From this study they reported the dissociation energy of the CdCl gas as \(2.11 \pm 0.03\) e.v. and \(2.17\) e.v. in two respective communications.

Herzberg and Stevenson\(^{103}\) gave molecular data for CdCl gas from which the value of \(S^0_{298.15} = 60.4 \pm 0.5\) was obtained. Using the value of 26.75 k.cal/mole for the heat of sublimation of cadmium and the heat of formation of ideal monoatomic chlorine\(^{104}\) 28.94 k.cal/mole, the values obtained for the heat of formation CdCl gas are \(-8.76\) k.cal/mole (from the dissociation energy value reported by Herzberg) and \(+7.39 \pm 0.69\) k.cal/mole (from Gaydon's value). These values are calculated employing the expression,\(^{105}\)

\[
D(MX) = -Qf(MX) - \Delta_s H(MX) + \Delta_s H(M) + Qf(X)
\]

where \(Qf(MX)\) - standard heat of formation of MX where MX is a monohalide of a metal
\(\Delta_s H(MX)\) - heat of vapourization of monohalide
\(\Delta_s H(M)\) - heat of sublimation of metal
\(Qf(X)\) - standard heat of formation of halide
Objective of the Study

The above description shows a wide difference in the values of the heat of formation for the molecule CdCl\(_2(g)\). In view of this, it was thought worthwhile to study the chemical transport reaction

\[
\text{Cd}(g) + \text{CdCl}_2(c) \rightarrow 20\text{CdCl}(g)
\]

at high temperatures and to obtain experimentally the value of \(\Delta H_{298}^0\) for CdCl\(_2(g)\).

Cadmium metal can be easily vaporized at the reaction temperatures (719-766°K) at which the dicloride CdCl\(_2\) has negligible vapour pressure. Hence during the transpiration study at the above temperatures, the vapour of cadmium has been passed over solid CdCl\(_2\) to obtain the gaseous monochloride.

Employing the heat content functions and entropies of CdCl\(_2(g)\), CdCl\(_2(c)\) and Cd\(_2(g)\) listed by Kelley and King\(^{106,107}\) and the heats of formation of Cd\(_2(g)\)\(^{104}\), CdCl\(_2(g)\)\(^{99}\) and CdCl\(_2(c)\)\(^{108}\), it is possible to calculate the amount of CdCl\(_2\) transported during the reaction. Alternatively, if the transported CdCl\(_2\) is determined experimentally the heat of formation CdCl\(_2(g)\) can be calculated.

In order to study the reaction

\[
\text{Cd}(g) + \text{CdCl}_2(c) \rightarrow 20\text{CdCl}(g)
\]  \hspace{1cm} (11)

the vapour pressure of Cd\(_2(g)\) in equilibrium with Cd\(_2(l)\) was studied.
3.1.1 Introduction

The results of mass spectrometric measurements indicate that only monoatomic molecules of Cd(g) are found in the vapour of cadmium. Barus determined the vapour pressure of cadmium by the boiling point method but the values were lower because of the impure metal used. After this, many workers employing the boiling point method have reported the vapour pressures of cadmium over Cd(l).

The studies have also been carried out by employing static methods and flow methods.

Summarizing the above work, Nesmeyanov pointed out that the values reported are either higher or lower because of either impure material or imperfections in the method. The reliable data for the vapour pressure of liquid cadmium are by Braune who used the boiling point method in the temperature range 663.9 - 833.1°C and flow method in the range 349.7-570.9°C and by Fogler and Rodeoush who employed the boiling point method. The values obtained in the present work are comparable with those of Braune who employed hydrogen as a carrier gas.
Materials

A] Cadmium metal supplied by Johnson Mathey (U.K.) 99.9% pure was turned carefully on a clean lathe. The shavings were degreased, dried completely and used.

B] Argon gas purified as described below was used as the carrier gas.

Apparatus and Procedure

The argon gas from the cylinder contains impurities such as oxygen, nitrogen, carbon dioxide and moisture etc. These impurities were removed by passing the gas through a purification train schematically shown in Fig. 1. The purification train consisted of glass bubblers (A) containing alkaline pyrogallol and (B) containing sulphuric acid, a calibrated flow meter (C) to regulate and measure the flow of gas and columns D, G containing calcium chloride and $P_2O_5$ respectively to remove moisture and long horizontally placed columns E and F containing sofnolite and anhydrene to remove $CO_2$. Finally the gas was allowed to pass through a tube (H) containing freshly reduced copper kept at $600^\circ C$. Boats containing calcium turnings, aluminium metal and titanium sponge$^{118}$ were kept at about $700^\circ C$ in a mullite tube (I) to remove traces of oxygen and nitrogen. Besides, freshly prepared manganous oxide$^{119}$ (U) was also used to remove traces of oxygen of about 1 ppm or less.
The vaporization of cadmium was carried out in a vycor tube (100 cms. long and 2 cms. inner diameter) placed in a Kanthal wound tube furnace which gave a constant temperature ($\pm 5^\circ$) between $623^\circ$K and $715^\circ$K over a zone 6.5 cm. in length. The temperature was attained by connecting the heating element to a variable voltage transformer which was connected to 230 v main source through a voltage stabiliser to maintain the constancy of the power supply. To keep the radiation losses at a minimum, the heating element was insulated with light magnesia refractory bricks (BAGSVIC). A chromel-alumel thermocouple calibrated at Al and Cu points and positioned in the annular space between the reaction tube and heating tube, served for measurement of temperatures. The thermal e.m.f. was read with a thermocouple test set supplied by W.G. Pye and Co.Ltd., England (Cat. No. 7556).

A vycor boat was used as container for the cadmium metal. The tube was completely flushed with argon gas. After attaining the required constant temperature and maintaining desired flow of argon gas, the boat containing weighed cadmium metal was introduced in the reaction zone from the downstream end. (Precautions were taken to avoid contamination of carrier gas with air, while inserting and removing the boat out of the flow system). The experiments were carried out for 2.6 hours. After completing the reaction the heating was stopped and the reaction tube was pushed in such a way that the boat was out of the temperature zone. The system was allowed to cool in an argon atmosphere. Then the boat was pushed into a glass capsule which was
immediately stoppered. The transported cadmium was found by weight loss measurement.

Transpiration runs with argon as carrier gas were carried out for 2.5 hours to study the vaporization of cadmium in the temperature range 623°-715°K. Preliminary runs for vaporization study at different flow rates showed that the effects of self diffusion and thermal diffusion were negligible at the flow rates employed in the experiments. The results of the experiments at different temperatures are given in Table I. The plot of log p vs 1/T has been shown in Figure 2. These data have been employed in the study of the equilibrium reaction (Section II of this Chapter).

3.1.3 Treatment of the data

To calculate vapour pressures of cadmium, the experimental weight loss data obtained in the temperature range 623°-715°K for cadmium were used. The free energy change was also calculated at experimental temperatures employing the equation

$$\Delta_f^0 = -RT \ln K \quad \ldots \quad (26)$$

To calculate the heat of vaporization at 298°K by second law method, the well-known vant Hoff's equation was used.

$$\frac{d \ln P}{d(1/T)} = \frac{-\Delta_H}{R} \quad \ldots \quad (28)$$

From the plot of logarithm of the equilibrium pressure versus the reciprocal of absolute temperature, the heat of vaporization was determined. (Fig.2)
### Table I

Vaporization of $\text{Cd}_{(l)} \rightleftharpoons \text{Cd}_{(g)}$ and Third Law Heats

<table>
<thead>
<tr>
<th>No.</th>
<th>Temp. $^\circ$K</th>
<th>Rate of flow of argon gas lit/hr.</th>
<th>Cd. metal transported mgs.</th>
<th>$P \times 10^4$ atm.</th>
<th>$\Delta F$ (-$\text{R} \ln K_p$)</th>
<th>$T \Delta f_{ef}$</th>
<th>$\Delta H_{298}$ K.cal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>623</td>
<td>2.70</td>
<td>11.0</td>
<td>3.5449</td>
<td>9.83</td>
<td>16.98</td>
<td>26.81</td>
</tr>
<tr>
<td>2.</td>
<td>636</td>
<td>2.72</td>
<td>15.0</td>
<td>4.7986</td>
<td>9.66</td>
<td>17.30</td>
<td>26.96</td>
</tr>
<tr>
<td>3.</td>
<td>647</td>
<td>2.88</td>
<td>28.6</td>
<td>7.7347</td>
<td>9.21</td>
<td>17.55</td>
<td>26.76</td>
</tr>
<tr>
<td>4.</td>
<td>666</td>
<td>2.88</td>
<td>61.2</td>
<td>12.4484</td>
<td>8.35</td>
<td>18.01</td>
<td>26.86</td>
</tr>
<tr>
<td>5.</td>
<td>689</td>
<td>2.52</td>
<td>72.6</td>
<td>25.0693</td>
<td>8.20</td>
<td>18.56</td>
<td>26.76</td>
</tr>
<tr>
<td>6.</td>
<td>715</td>
<td>2.70</td>
<td>149.0</td>
<td>48.0198</td>
<td>7.58</td>
<td>19.19</td>
<td>26.77</td>
</tr>
</tbody>
</table>

Duration of Experiment 2.5 hrs.

A.V. 26.82 $\pm 0.1$
FIG. 2. PLOT OF OR VAPORIZATION OF Cd
3.1.4 Results and Discussion

The vapour pressure equation obtained by the least square method can be represented as

\[
\log P = \frac{-5317.1 \pm 150.6}{T} + 5.101 \pm 0.23
\] (44)

The slope of this curve gave the second law heat 
\[\Delta H_{669^\circ K} = 24.33 \pm 0.15 \text{ k.cal/mole}.\] This represents the mean value over the temperature range studied and does not include the effect of \(\Delta C_p\). According to Stull and Sinke\(^{104}\) the change in \(C_p\) for cadmium metal is -2.13 cal. This difference of \(C_p\) value when integrated between the limits of 298\(^\circ\)K and 669\(^\circ\)K gives a value of 0.79 k.cal. Employing Kirchoff's equation,

\[
\Delta H_T = \Delta H_0 + \int_{669}^{298} \Delta C_p \, dT
\] (45)

The value for \(\Delta H_{298}\) of sublimation is obtained as follows:

\[
\Delta H_{298} = \Delta H_{669} + \int_{669}^{298} -2.31 \, dT = 24.33 \pm 0.15 + 0.79 = 25.12 \pm 0.16 \text{ k.cal/mole}
\]

Adding the heat of fusion 1.46 k.cal/mole (Stull and Sinke\(^{104}\)) a value of 26.57 k.cal/mole is obtained for \(\Delta H^{\circ}_{298}\). The third law heat has been calculated from the equation

\[
\Delta H_T^{\circ}_{\text{ref}} = \Delta F^{\circ} - T\Delta fef
\] (41)

employing \(\Delta fef\) values given by Stull and Sinke\(^{104}\). These
calculations yield a third law heat as $26.82 \pm 0.15$ k.cal/mole. This value agrees well with that reported by Stull and Sinke\textsuperscript{104} (26.78 k.cal/mole).

3.1.5 **Entropy of vaporization**

The entropy of vaporization was calculated from the least square constant and was found to be $23.36 \pm 0.23$ e.u.
Section II

Equilibrium study of the reaction

\[ \text{Cd}_2(g) + \text{CdCl}_2(c) \rightleftharpoons 2\text{CdCl}_2(g) \] at high temperatures.

3.2.1 Introduction

The equilibrium reaction between gaseous cadmium metal and CdCl₂ solid may be understood by considering the following reactions,

\[ \text{Cd}_2(g) + \text{CdCl}_2(c) \rightleftharpoons 2\text{CdCl}_2(g) \] (11)

\[ \text{CdCl}_2(c) = \text{CdCl}_2(g) + \frac{1}{2}\text{Cl}_2(g) \] (46)

The vaporization of CdCl₂(c) was also studied at high temperatures using argon as carrier gas, no chlorine was observed in the exit gases, indicating that CdCl₂(c) did not dissociate. Hence the reaction represented by eqn. (46) can be neglected. Preliminary experiments with CdCl₂(c) in the temperature range 719°-766°K (temperatures employed in the present work), showed no vaporization of dichloride. However, when Cd₂(g) was passed over CdCl₂(c) in this temperature range, a loss in weight of CdCl₂(c) was observed. The reaction was therefore studied in detail and \( \Delta H_{298} \) for CdCl₂(g) was obtained.
3.2.2 Experimental

a) Materials

1) Cadmium metal (A.R. grade, supplied by M/s. Johnson Mathey Ltd., U.K.) was used.

2) Cadmium chloride (CdCl₂·xH₂O) crystals (A.R., B.D.H.). This was dehydrated in a stream of gaseous hydrochloric acid at 250°C for about 2 hours using purified nitrogen as a carrier gas. The dichloride was chemically analysed for chloride and cadmium by standard methods of analysis. The purity was found to be more than 99.9%. The anhydrous CdCl₂ was prepared fresh for every experiment.

3) Argon purified as described earlier was used.

b) Apparatus and Procedure

The reaction was studied in a special tube furnace (Fig. 3) wound with kanthal heating elements. The furnace could give two constant temperature zones K₁ and K₂ each nearly 8 cm. long and with a temperature variation of ±3°C. This was necessary to prevent the condensation of cadmium vapours in the middle of the reaction tube. The constant temperature zones were long enough to accommodate two vycor boats (C and D). The temperature was attained in both the zones by connecting the heating elements to variable voltage transformers, which were connected to 230 v main source through voltage stabilisers to maintain the constancy of power supply. To minimise the radiation losses, the heating element was insulated with light refractory bricks (BAGSVIC), temperature was measured with chromel-alumel thermocouple (calibrated, as described in Section I of this Chapter.)
A. RADIATION SHIELDS
B. BOATS CONTAINING METALHALIDE AND METAL
C. B24 MALE GLASS JOINTS
D. THERMOCOUPLE SHEATHS
E. VARIACS CONNECTED THROUGH VOLTAGE STABILIZER
F. CONSTANT TEMPERATURE ZONES

3. FURNACE FOR THE STUDY OF THE EQUILIBRIUM REACTION

\[
\text{Cd}(g) + \text{CdCl}_2(c) \rightleftharpoons 2\text{CdCl}_1(g)
\]
A transluscent silica tube of 100 cm in length and 2 cm I.D. was employed to study the reaction. The reaction tube was ground at either ends to give suitable joints. The system was thus made gas tight. When the desired constant temperature in the reaction zone was attained, the argon rate was regulated to the desired value and the experiment was started by pushing the vycor boats containing metal and the metal dichloride in their respective zones. After continuing the run for a definite period (2.5 hours), the heating was stopped and the reaction tube was pushed in such a way that both the boats were out of their temperature zones. The system was then allowed to cool in an argon atmosphere, after which boats were taken out and weighed.

3.2.3 Effect of flow of argon gas

The equilibrium flow rates were determined by changing the argon flow rates and keeping the cadmium metal and cadmium dichloride at constant temperatures of 623°K and 736°K respectively. The results are given in Table II and figure 4. The linear portion indicates the equilibrium flow rates.

3.2.4 Identification of gaseous products

In a few experiments, the condensate deposited on a silica cold finger (introduced from the down-stream end in the reaction tube) was examined. It showed the presence of the metal dichloride. Since at these temperatures (719°K-766°K) CdCl₂ has negligible vapour pressure, its presence on the cold finger can be attributed to the disproportionation of the monohalide according to the following reaction:
Table II
Effect of flow Rate on the Reaction Cd\(_2\) \(\rightarrow\) CdCl\(_2\) \(\Rightarrow\) 2CdCl\(_\text{g}\)

<table>
<thead>
<tr>
<th>No.</th>
<th>Rate of flow of Argon gas lit/hr</th>
<th>Cd(_\text{g}) passed (mgs)</th>
<th>CdCl(_\text{2}) transported (mgs)</th>
<th>P Cd(_\text{g}) x 10(^4) atm</th>
<th>P CdCl x 10(^4) atm</th>
<th>Kp x 10(^3)</th>
<th>-RTlnK k.cal./mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>3.45</td>
<td>7.8</td>
<td>8.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>5.25</td>
<td>11.8</td>
<td>10.0</td>
<td>2.3471</td>
<td>5.0761</td>
<td>1.09781</td>
<td>10.01</td>
</tr>
<tr>
<td>3.</td>
<td>6.00</td>
<td>13.0</td>
<td>12.0</td>
<td>2.0458</td>
<td>5.3304</td>
<td>1.3886</td>
<td>9.67</td>
</tr>
<tr>
<td>4.</td>
<td>6.75</td>
<td>15.0</td>
<td>13.0</td>
<td>2.2651</td>
<td>5.1381</td>
<td>1.1655</td>
<td>9.93</td>
</tr>
<tr>
<td>5.</td>
<td>7.20</td>
<td>15.6</td>
<td>15.0</td>
<td>1.9344</td>
<td>5.5578</td>
<td>1.5968</td>
<td>9.47</td>
</tr>
<tr>
<td>6.</td>
<td>8.25</td>
<td>20.6</td>
<td>15.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Duration of each run is 2.5 hours. Reaction Temp. 740\(^0\)K. Cd\(_\text{g}\) generation temp 625\(^0\)K
\[ 2 \text{CdCl}_\text{(g)} \rightarrow \text{Cd}_\text{(g)} + \text{CdCl}_2 \text{(c)} \]  \hspace{1cm} (47)

The experiments were carried out at different temperatures in the range 719°-766°K. The results are tabulated in Table III and plot of log $K_P$ versus $1/T$ is shown in Figure 5.

3.2.5 Treatment of the data

The partial pressures of $\text{Cd}_\text{(g)}$ and $\text{CdCl}_\text{(g)}$ were calculated as follows:

\[ P_{\text{CdCl}_\text{(g)}} = n_a \frac{HTr}{V_r} \]  \hspace{1cm} (48)

\[ P_{\text{Cd}_\text{(g)}} = n_b \frac{HTr}{V_r} \]  \hspace{1cm} (49)

where $n_a$ and $n_b$ are the number of moles of CdCl and Cd respectively. From the loss in weight ($\Delta W$) $n_a$ and $n_b$ are calculated as

\[ n_a = \frac{2 \Delta W \text{CdCl}_2}{\text{Mol.wt.CdCl}_2} \]

\[ n_b = \frac{\Delta W \text{Cd}}{\text{Mol.wt.Cd}} - \frac{\Delta W \text{CdCl}_2}{\text{Mol.wt.CdCl}_2} \]

The equilibrium constant for the reaction was calculated by substituting the pressures of CdCl and Cd in the expression

\[ K_p = \frac{[\text{PcdCl}]^2}{[\text{PCd}]} \]  \hspace{1cm} (50)

The free energy and heat of reaction at various temperatures were calculated employing the equation
### Table III

Transpiration Data and Related Third Law Heats for the reaction Cd\(_{(g)}\) + CdCl\(_2(c)\) ⇌ 2CdCl\(_{(g)}\)

<table>
<thead>
<tr>
<th>No.</th>
<th>Temp. (o_K)</th>
<th>Argon gas passed lit/hr</th>
<th>Cd passed mgs.</th>
<th>CdCl(_2) transported mgs.</th>
<th>(P \text{ CdCl}_2) (10^4) atm.</th>
<th>(-\log K_p)</th>
<th>(\Delta F) ((-RT\ln K_p)) k.cal/mole</th>
<th>(+\Delta H_{298}) CdCl(_2) k.cal/mole</th>
<th>(\Delta H_{298}) CdCl(_{(g)}) k.cal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>719</td>
<td>2.72</td>
<td>14.6</td>
<td>9.0</td>
<td>3.5311</td>
<td>+3.3722</td>
<td>11.61</td>
<td>47.03</td>
<td>-9.70</td>
</tr>
<tr>
<td>2.</td>
<td>733</td>
<td>2.76</td>
<td>15.0</td>
<td>12.0</td>
<td>1.6390</td>
<td>3.0492</td>
<td>9.99</td>
<td>46.05</td>
<td>-10.19</td>
</tr>
<tr>
<td>3.</td>
<td>740</td>
<td>2.72</td>
<td>15.0</td>
<td>13.2</td>
<td>5.1790</td>
<td>2.9158</td>
<td>9.87</td>
<td>46.32</td>
<td>-10.10</td>
</tr>
<tr>
<td>4.</td>
<td>755</td>
<td>2.76</td>
<td>14.8</td>
<td>15.0</td>
<td>5.7997</td>
<td>2.7203</td>
<td>9.39</td>
<td>45.71</td>
<td>-10.38</td>
</tr>
<tr>
<td>5.</td>
<td>766</td>
<td>2.76</td>
<td>15.2</td>
<td>18.2</td>
<td>7.0373</td>
<td>2.4103</td>
<td>8.45</td>
<td>45.80</td>
<td>-10.32</td>
</tr>
</tbody>
</table>

A.V. = -10.12 †

Duration of experiment 2.5 hrs.
FIG. 5 PLOT OF $\log K_p$ vs $\frac{1}{T}$ FOR THE REACTION

$$Cd_{(g)} + CdCl_{2(c)} \rightleftharpoons 2CdCl_{(g)}$$
\[
\Delta F^0 = -kT \ln k
\]  
\[\frac{\Delta H_{298}^0}{T} = -\ln P \frac{F^0_T - H^0_{298}}{T} \text{ (product)}
\]  
\[+ \frac{F^0_T - H^0_{298}}{T} \text{ (reactants)}
\]  

3.2.6 Results and Discussion

The free energy functions for products and reactants were calculated from the heat and entropy values given by Kelley. The data have been summarized in Table III. Employing the van't Hoff's equation, the heat of reaction \( \Delta H \) has been determined from the plot of \( \log K_p \) versus \( 1/T \) (Fig. 5). The slope of the line obtained by the method of least squares gave the heat of reaction \( \Delta H_{742} = 48.87 \text{ k.cal/mole} \). This value of \( \Delta H \) represents the mean over the temperature range studied and does not include the \( C_p \) values. The value for \( \Delta H_{298} \) could be calculated from the knowledge \( \Delta H_{742} \) and \( C_p \) values. According to Kelley the value for the change in \( C_p \) is 9.97 cal.deg.\(^{-1}\) when this value is integrated between the limits 298 and 742\(^0\)K a value of 4.42 is obtained. Thus \( H_{298} \) is 53.29 \( \pm \) 0.5 k.cal/mole. The third law heat has been calculated at desired temperatures from heat contents and entropies given by Kelley and King. The experimental value for the heat of reaction is 46.16 k.cal/mole.

Heat of formation of CdCl\(_2(g)\)

The heat of formation of CdCl\(_2(g)\) has been calculated as follows:
\[ \Delta H_{298} = 2 \Delta H_{298} \text{CdCl}_2(g) - \Delta H_{298} \text{Cd}(g) - \Delta H_{298} \text{CdCl}_2(c) \]  

Hence

\[ \Delta H_{298} \text{CdCl}_2(g) = \frac{1}{2} [\Delta H_{298} + \Delta H_{298} \text{CdCl}_2(c) + \Delta H_{298} \text{Cd}(g)] \]

The second law value for $\Delta H_{298}$ is $-6.57 \pm 0.33$ and that obtained from third law is $-10.12 \pm 0.5$ k.cal/mole. The heats of formation of Cd(g) and CdCl$_2$(c) were taken from Stull and Sinke\textsuperscript{104} and Brewer\textsuperscript{108} et al, respectively. The experimentally obtained value for CdCl$_2$(g) compared well with that calculated from dissociation energy reported by Herzberg ($\Delta H_{298} = -8.76$ k.cal/mole). The difference in third law heat and second heat can be attributed to temperature dependant errors.

**Entropy of the reaction**

The entropy of the reaction can be calculated either from the intercept of the plot of log $K_p$ versus $1/T$ or by substituting the value for $\Delta H_{742}$ and $\Delta F_{742}$ in the equation

\[ \Delta F_T = \Delta H_T - T \Delta S_T \]

From this a value of $52.61 \pm 0.68$ e.u. at 742\textdegree K was obtained for the entropy of the reaction.

The present work was carried out in a rather limited range of temperatures because cadmium dichloride has negligible vapour pressure only in the present temperature range (719\textdegree - 766\textdegree K). Beyond 800\textdegree K CdCl$_2$ starts vaporizing appreciably. In order to avoid complications the study was conducted in the narrow temperature range of 719\textdegree - 766\textdegree K in which the vapour of cadmium metal could be easily passed over solid CdCl$_2$. 
Thermodynamic data for vapour pressure of cadmium metal and equilibrium reaction,
\[ \text{Cd}(g) + \text{CdCl}_2(c) \rightleftharpoons 2\text{CdCl}(g) \]

| \( \Delta H_{\text{sub Cd}} \) at 669\(^\circ\)K | 24.33 ± 0.15 k.cal/mole (II Law) |
| \( \Delta S_{\text{sub Cd}} \) at 669\(^\circ\)K | 23.36 ± 0.23 e.u. (II Law) |
| \( \Delta H_{\text{sub Cd}} \) at 298\(^\circ\)K | 26.57 ± 0.15 k.cal/mole (II Law) |
| \( \Delta H_{\text{sub Cd}} \) at 298\(^\circ\)K | 26.82 ± 0.14 k.cal/mole (III Law) |
| \( \Delta H_{r} \) at 742\(^\circ\)K | 48.87 ± 0.50 k.cal/mole (II Law) |
| \( \Delta H_{r} \) at 298\(^\circ\) | 53.29 ± 0.50 k.cal/mole (II Law) |
| \( \Delta H_{F} \) at 298\(^\circ\)K | 46.18 ± 0.85 k.cal/mole (III Law) |
| \( \Delta S_{E} \) at 742\(^\circ\)K | 52.61 ± 0.68 e.u. |
| \( \Delta H_{F298} \) \text{CdCl}(g) | -6.57 ± 0.33 k.cal/mole (II Law) |
| \( \Delta H_{F298} \) \text{CdCl}(g) | -10.12 ± 0.49 k.cal/mole (III Law) |