# Thermodynamics of Vapor Phase Dissociation of Dimeric Aluminum Chloride

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**The equilibrium constants for the reaction $Al_2Cl_6(g) \rightleftharpoons 2AlCl_3(g)$ have been determined by vapor density measurement over the region 240° to 550° C. Both a tin manometer and glass-bourdon gage were used as null point indicators and gave essentially the same results. The enthalpy for this dissociation reaction, $\Delta H_{d_{298}}$, was $29.4_1$ kcal. per mole by third law and $29.5_5$ kcal. per mole by second law calculations. The results confirm those of previous workers and indicate that the free-energy functions calculated for this reaction are reliable.**

THE DISSOCIATION of dimeric aluminum chloride in the vapor state was studied about 30 years ago by two groups—Fischer, Ralhfs, and Benze (*3*), and Smits and Meijering (*5*)—by determination of the vapor density at various temperatures, and from these data they calculated the equilibrium constants and thermodynamic constants for the reaction, $Al_2Cl_6(g) \rightleftharpoons 2AlCl_3(g)$. Fischer *et al.*, using a tin manometer, observed appreciable residual pressures, perhaps owing to contamination of the sample. Smits and Meijering used a quartz-bourdon gage and do not report any residual gas pressure; however, they report only a few points, and their calculations have been found to be in error.

Recent calculations performed in the Dow Thermal Research Laboratory for the JANAF Tables (*4*) have indicated that, although second law plots of Fischer's data are fairly linear, third law calculations involving free energy functions show a drift in the values of $\Delta H_{d_{298}}$ with temperature. This indicates either that the free energy functions of the dimer and monomer of aluminum chloride are inexactly known, or that the vapor density data are in error. To preclude the latter possibility, the experiments using improved vacuum techniques and high purity aluminum chloride were rerun to either confirm or alter the previous results.

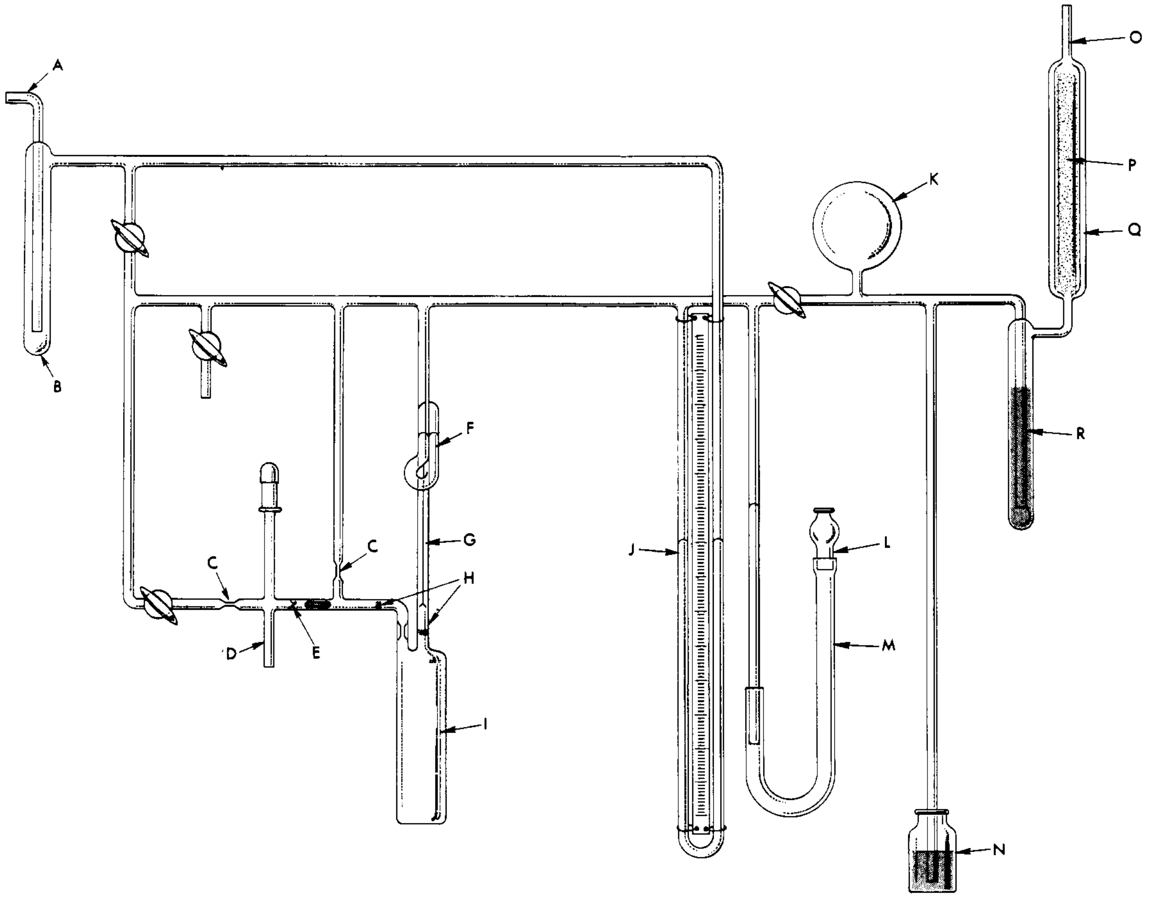

Figure 1. Vapor density apparatus

A. To vacuum system
B. Liquid nitrogen trap (−196° C.)
C. Constrictions for sealing off
D. Sample holder
E. Break seal
F. Tin manometer
G. Capillary tubing
H. Graded seal: Vycor to borosilicate glass
I. Vycor bulb
J. Mercury manometer
K. 500-ml. flask
L. Mercury leveling bulb
M. Heavy-walled Tygon tubing
N. Mercury safety valve
O. Nitrogen source
P. Copper filings
Q. Furnace
R. Silica gel trap (−78° C.)

## EXPERIMENTAL

**Apparatus.** In the first two experiments, a device very similar to that described by Datz, Smith, and Taylor (*2*) was used with some modification (Figure 1). A 250-cc. cylindrical Vycor bulb (*I*) was attached to the tin manometer by capillary tubing (*G*). The total volume of the manometer (*F*) from the top of the bulb to the surface of the tin was 3.27 cc. or about 1.3% of the total volume. Both sides of the molten tin could be evacuated before an experiment to less than 1 micron, and nitrogen purified over hot copper filings (*P*) and silica gel (*R*) at −78° C. was used to maintain the null point. The actual pressure was read on a mercury manometer (*J*) by a cathetometer.

The last two experiments were carried out with a borosilicate glass bourdon gage (Kern-Springham, No. K-9205) in place of the tin manometer. By the use of over 1 meter total optical lever, one can observe the null point to within 0.2 torr. The Vycor bulb was immersed in a liquid solder bath contained in a stainless steel cylinder. Three chromel-alumel thermocouples in 5-mm. borosilicate glass tubes were wired to the bulb and placed 1 inch from the top, 1 inch from the bottom, and at the center of the bulb. These were calibrated relative to a Leeds-Northrup standardized platinum resistance thermometer. The manometer temperature was held at 300° C. in a glass core furnace which dipped into the solder of the bath. Two iron-constantan thermocouples were placed in this furnace, one at the tin manometer (or at the beginning of the glass spiral) and the second just above the solder of the bath.

**Sample.** The aluminum chloride consisted of reagent-grade material which had been sublimed through charcoal under vacuum. In Experiments 1 and 2, a rather elaborate device (*D*) including the stopcock to the left and the break seal (*E*) was used to introduce a high purity sample into the Vycor bulb (Figure 1). This sample device was initially evacuated, filled with nitrogen, and removed from the apparatus. In a dry box, a weighed sample of aluminum chloride was put into this sample device and it was again sealed into the apparatus. The Vycor bulb was heated and evacuated. The sample was evacuated at −78° C. for 30 minutes, sublimed into the Vycor bulb, and sealed off. Unfortunately, the sample holder was not preheated during evacuation so it contained adsorbed gases which reacted with the aluminum chloride and left a residue. In Experiments 3 and 4, a simpler and more satisfactory method was used for sample injection consisting of successive sublimation through several small bulbs. In both sets of experiments, the sample size was calculated from pressure measurements before and after the experiment at low temperatures where essentially only dimer is present. The volume of the Vycor bulb was determined after the experiment by calibration with water.

**Procedure.** The reagent grade tin for the manometer was heated in hydrogen just below its melting point; then it was melted down under vacuum and heated at 500° C. for 24 hours. Even after this treatment, the tin below the surface was not shiny but appeared rough and discolored next to the glass tubing. The procedure with the glass-bourdon gage simply involved heating the whole apparatus several hours under vacuum.

Once the furnace was moved into position, the nitrogen was added through a needle valve (*O*) or removed through the vacuum system (*A*) as required to maintain a zero pressure differential across the manometer. It generally required at least 2 hours for the entire system to come to thermal equilibrium after a temperature change, but thereafter the temperature was controlled to within a few tenths of a degree Centigrade by a time-proportional Honeywell-Pyrovane controller.

Table I. Equilibrium Constant Determination for the Dissociation Reaction $Al_2Cl_6(g) \rightleftarrows 2AlCl_3(g)$ as a Function of Temperature

| Temp., ° K. | Pressure, Mm. | $M_B$, Mmole | $K_p$, Mm. |
|---|---|---|---|
| Experiment 1[a] | | | |
| $V_B = 251.124$; $M_T = 1.5131$ mmoles; $P_r = 1.2$ mm. | | | |
| 513.45 | 192.20 | 1.4959 | 0.04485 |
| 627.90 | 243.30 | 1.4918 | 2.057 |
| 638.41 | 248.60 | 1.4916 | 2.619 |
| 692.36 | 283.10 | 1.4888 | 12.85 |
| 723.98 | 308.20 | 1.4872 | 29.41 |
| 764.80 | 349.30 | 1.4843 | 84.72 |
| 802.60 | 393.80 | 1.4811 | 197.8 |
| Experiment 2[a] | | | |
| $V_B = 251.147$; $M_T = 1.5347$ mmoles; $P_r = 1.2$ mm. | | | |
| 519:39 | 197.40 | 1.5177 | 0.05645 |
| 523.33 | 198.50 | 1.5177 | 0.02931 |
| 643.13 | 255.8 | 1.5139 | 3.458 |
| 671.29 | 273.9 | 1.5128 | 8.202 |
| 671.64 | 273.6 | 1.5125 | 7.896 |
| 686.88 | 283.9 | 1.5121 | 11.66 |
| 722.50 | 314.9 | 1.5101 | 34.08 |
| 770.75 | 364.5 | 1.5070 | 109.1 |
| 819.75 | 426.6 | 1.5032 | 313.9 |
| Experiment 3[b] | | | |
| $V_B = 251.313$; $M_T = 1.3621$ millimoles; $P_r = 5.25$ mm. | | | |
| 525.76 | 177.5 | 1.3466 | 0.07553 |
| 682.52 | 249.5 | 1.3438 | 9.496 |
| 724.95 | 280.9 | 1.3412 | 31.15 |
| 773.22 | 325.7 | 1.3390 | 100.4 |
| 825.83 | 387.6 | 1.3362 | 323.6 |
| $M_T^c = 1.3380$ millimoles; $P_r = 6.25$ mm. | | | |
| 512.94 | 169.6 | 1.3235 | 0.02813 |
| 722.02 | 274.0 | 1.3182 | 28.84 |
| 779.22 | 327.1 | 1.3157 | 116.3 |
| 818.90 | 373.6 | 1.3137 | 283.8 |
| Experiment 4[b] | | | |
| $V_B = 251.313$; $M_T = 0.5127$ millimoles; $P_r = 0$ | | | |
| 525.47 | 66.9 | 0.5137 | 0.0005065 |
| 525.86 | 67.1 | 0.5071 | 0.0466 |
| 669.74 | 94.3 | 0.5056 | 5.660 |
| 670.86 | 94.3 | 0.5057 | 5.533 |
| 673.13 | 95.0 | 0.5056 | 6.024 |
| 720.55 | 111.4 | 0.5058 | 13.05 |
| 771.86 | 133.7 | 0.5037 | 93.27 |
| 821.61 | 159.6 | 0.5025 | 287.7 |

[a] Tin manometer. [b] Bourdon gage. [c] Corrected value for $M_T$ after a second heating cycle.

## RESULTS

**Calculations.** The calculation of vapor density required a knowledge of the bulb volume, $V_B$, the gas pressure $P$, the temperature of the bulb, $T_B$, and the number of moles of $Al_2Cl_6$ in the bulb at that temperature, $M_B$. Pressure, temperature, and volume were measured directly, whereas the number of moles in the bulb was calculated

Table II. Second Law Calculations of Enthalpy and Entropy for the Dissociation Reaction $Al_2Cl_6(g) \rightleftarrows 2AlCl_3\ (g)$ from the Equation, Log $K_{p(atm)} = -\Delta H_d/2.303RT + \Delta S_d/2.303$

| Expt. No. | Intercept[a] | Slope[a] | $T$, ° K. | $\Delta \bar{H}_d$ | $\Delta \bar{S}_d$ | $\Delta H_{d_{298}}$ | $\Delta S_{d_{298}}$ |
|---|---|---|---|---|---|---|---|
| 1 | 6.5660 | 5756.3 | 704.58 | $26.3_4 \pm 0.4$ | $30.0_4 \pm 0.6$ | $27.9_6$ | $33.4_7$ |
| 2 | 6.7968 | 5890.3 | 720.78 | $26.9_5 \pm 0.3$ | $31.1_0 \pm 0.4$ | $28.6_4$ | $34.6_2$ |
| 3 | 6.9706 | 6062.8 | 740.86 | $27.7_4 \pm 0.1$ | $31.9_0 \pm 0.1$ | $29.5_1$ | $35.5_2$ |
| 4 | 7.1723 | 6237.2 | 737.94 | $28.5_4 \pm 0.2$ | $32.8_2 \pm 0.3$ | $30.3_0$ | $36.4_3$ |
| Combined[b] | 6.9894 | 6072.5 | 739.64 | $27.7_9 \pm 0.4$ | $31.9_8 \pm 0.5$ | $29.5_5$ | $35.6_0$ |
| Fischer *et al.*[c] | 7.1656 | 6201.0 | 713.36 | $28.3_7 \pm 0.4$ | $32.7_9 \pm 0.6$ | $30.0_3$ | $36.2_6$ |
| Smits and Meijering[c] | 7.0112 | 6041.8 | 735.22 | $27.6_5 \pm 0.7$ | $32.0_8 \pm 0.9$ | $29.3_9$ | $35.6_8$ |

[a] These apply to the equation log $K_{p(\text{atm.})}$ = –Slope/$T$ + Intercept. [b] This involved using all the points except the three below 670° K. in the program to give the best least squares fit. The lowest three points were rejected because of their high uncertainty. [c] Smits and Meijering's results are based on six points. Fischer *et al.*'s on 17, and the authors' on 24.

from the total number of moles of aluminum chloride, $M_T$, corrected for the number present in the manometer system. Since the manometer system comprised only 1.3% or less of $V_B$, this correction was not large. The number of moles of aluminum chloride in the manometer expressed as $Al_2Cl_6$ was calculated by assuming a linear temperature gradient across the manometer capillary and by using the equilibrium constant expression from Smits and Meijering's work (*5*).

$$\log K\ (\text{atm.}) = -\frac{6041.8}{T} + 7.0112 \qquad (1)$$

The total number of aluminum chloride moles in the system, $M_T$, expressed as $Al_2Cl_6$ was calculated by means of the ideal gas law using vapor pressure data at around 250° C. at which essentially only dimer is present.

An initial calculation indicated that at this temperature approximately 1.5% monomer is present. Thus, a value of $K_p$ at this temperature was determined from an initial second law plot and $M_T$ was corrected for the amount of monomer present. Then this new value of $M_T$ was used in the final calculation. The total number of gas moles in the bulb, $m$, is determined from the equation

$$m = \frac{PV_B}{RT_B} \qquad (2)$$

If $n_1$ is the number of moles of monomer in the bulb and $n_2$ the number of moles of dimer, then

$$n_1 + n_2 = m \qquad (3)$$

and $M_B$, the number of moles of aluminum chloride (expressed as $Al_2Cl_6$) in the bulb, is

$$\frac{n_1}{2} + n_2 = M_B \qquad (4)$$

Solving for $n_1$ and $n_2$ gives

$$n_1 = 2(m - M_B) \qquad (5)$$

$$n_2 = 2M_B - m \qquad (6)$$

The respective partial pressures are

$$p_1 = P\frac{n_1}{m} \qquad (7)$$

$$p_2 = P\frac{n_2}{m} \qquad (8)$$

and the equilibrium constant for the dissociation reaction is

Table III. Third Law Calculations of Enthalpy of the Dissociation Reaction $Al_2Cl_6(g) \rightleftarrows 2AlCl_3(g)$

| Temp., ° K. | $-\Delta(F_T - H_{298})/T$, Cal./Deg. | $-R\ln K_{p(\text{atm.})}$, Cal./Deg. | $\Delta H_{d_{298}}$, Kcal./Mole |
|---|---|---|---|
| | Experiment 1 | | |
| 627.90 | 37.602 | 11.748 | $29.10_3$ |
| 638.41 | 34.567 | 11.268 | $29.26_1$ |
| 692.36 | 34.388 | 8.107 | $29.42_2$ |
| 723.98 | 34.385 | 6.763 | $29.50_0$ |
| 764.80 | 34.155 | 4.360 | $29.45_6$ |
| 802.60 | 34.036 | 2.675 | $29.46_4$ |
| | | | av. $29.36_8 \pm 0.06$ |
| | Experiment 2 | | |
| 643.13 | 34.551 | 10.716 | $29.11_2$ |
| 671.29 | 34.457 | 9.000 | $29.17_2$ |
| 671.64 | 34.456 | 9.075 | $29.23_7$ |
| 686.88 | 34.406 | 8.300 | $29.33_4$ |
| 722.50 | 34.290 | 6.169 | $29.23_2$ |
| 770.75 | 34.136 | 3.858 | $29.28_4$ |
| 819.75 | 33.983 | 1.757 | $29.29_8$ |
| | | | av. $29.23_8 \pm 0.03$ |
| | Experiment 3 | | |
| 671.74 | 34.456 | 9.453 | $29.49_6$ |
| 682.52 | 34.420 | 8.709 | $29.43_6$ |
| 722.02 | 34.291 | 6.501 | $29.45_3$ |
| 724.95 | 34.282 | 6.348 | $29.45_5$ |
| 773.22 | 34.128 | 4.022 | $29.49_8$ |
| 779.22 | 34.109 | 3.730 | $29.48_5$ |
| 818.90 | 33.985 | 1.947 | $29.43_3$ |
| 825.83 | 33.964 | 1.697 | $29.44_9$ |
| | | | av. $29.46_3 \pm 0.01$ |
| | Experiment 4 | | |
| 669.74 | 34.462 | 9.737 | $29.60_2$ |
| 670.86 | 34.459 | 9.782 | $29.67_9$ |
| 673.13 | 34.451 | 9.603 | $29.66_1$ |
| 720.55 | 34.296 | 6.729 | $29.56_1$ |
| 771.86 | 34.132 | 4.169 | $29.56_2$ |
| 821.61 | 33.977 | 1.930 | $29.50_2$ |
| | | | av. $29.59_5 \pm 0.03$ |
| Average Values of $\Delta H_{d_{298}}$ | | | |
| Vrieland and Stull | | | 29.41±0.03 |
| Fischer, Rahlfs, and Benze | | | 29.45±0.03 |
| Smits and Jeijering | | | 29.23±0.04 |
| | | | av. 29.36±0.07 |

$$K_p = \frac{p_1^2}{p_2} = \frac{4P(m - M_B)^2}{m(2M_B - m)} \qquad (9)$$

With the tin manometer in the system, the residual gas pressure at room temperature amounted to only 1.2 torr which was merely subtracted from the observed pressure. However, in Experiment 3, with the glass-bourdon gage, the residual pressure was 5.25 torr and increased to 6.25 torr after a second heating cycle. This was assumed to result from a residual gas and the correction factor involved the ratio of measured temperature to room temperature. This residual pressure could have been due to a shift of the zero position of the bourdon gage, which was considered less likely and did not yield appreciably different results. In Experiment 4, the bourdon system gave no residual pressure.

**Thermodynamic Constants.** The vapor density data and the equilibrium constants calculated from them are given in Table I for the four experiments. Table II shows the results of least squares calculations based on the second law equation

$$\log K_p = \frac{-\Delta H_d}{2.303RT} + \frac{\Delta S_d}{2.303R} \qquad (10)$$

and includes values of $\Delta H_{d_{298}}$ and $\Delta S_{d_{298}}$ calculated from heat capacity data given in the JANAF Tables (*4*). Table III contains the results of third law calculations of $\Delta H_{d_{298}}$ based on the equation

$$\frac{\Delta H_{d_{298}}}{T} = -R\ln K_p - \Delta\left[\frac{(F - H_{298})}{T}\right] \qquad (11)$$

where the free energy functions also are taken from the JANAF Tables and are based on known or estimated parameters of the monomer and dimer. The results of Fischer, Rahlfs, and Benze (*3*) and Smits and Meijering (*5*) also were evaluated by the same programs and are included in Tables II and III.

## DISCUSSION AND CONCLUSIONS

The accuracy of the calculated values of $K_p$ and $\Delta H_d$ can be estimated from the expected uncertainties in the measured values of temperature, pressure, and volume. Taking the uncertainty in temperature as 0.15%, in volume as 0.2%, and in pressure as 0.08 to 0.05% for pressures of 240 to 390 torr, respectively, standard deviations are estimated in $K_p$ of 2.4% at 825° K., 8.9% at 670° K., and 16.6% at 627° K. The uncertainty increases rather rapidly at decreasing temperatures because of the factor $(m - M_B)^2$ in Equation 9.

The determination of $\Delta \bar{H}_d$ by the van't Hoff equation

$$\Delta \bar{H}_d = \frac{RT_1T_2}{T_1 - T_2} \ln (K_1/K_2) \qquad (12)$$

can lead to rather larger uncertainties in $\Delta \bar{H}_d$ not only from errors in the equilibrium constants $K_1$ and $K_2$ but because $\Delta H_d$ itself often varies with temperature (*1*).

In the temperature range 670° to 825° K., an uncertainty is estimated in $\Delta \bar{H}_d$ from Equation 12 of ±0.7 kcal. per mole. If the lowest three points (at 627°, 643°, and 638° K.) are added to the least squares calculation of the combined results, the value of $\Delta H_{298}$ drops by 0.6 to 28.78 kcal. per mole. No doubt these three points are responsible for the low values of $\Delta H_{298}$ in Experiments 1 and 2 as compared with 3 and 4

In the third law calculations, the deviation in $\Delta H_{d_{298}}$ is much less sensitive to an uncertainty in the equilibrium constants because the term $R \ln K_p$ in Equation 11 is small relative to the entropy term. For example, at 722° K. the error in $K_p$ is 5.0% which gives $RT \ln K_p = 4.46 \pm 0.07$ kcal. per mole. The error in $\Delta H_{d_{298}}$ related to this term alone is thus ±0.07 kcal. per mole. Since the free energy functions are based on known and estimated vibration frequencies, there is no way to estimate their uncertainties.

The results of the third law calculations indicate that $\Delta H_{d_{298}}$ is constant to within around ±0.03 kcal. per mole for a given experiment and the agreement is to within ±0.03 kcal. per mole among the four experiments. The average value of $\Delta H_{d_{298}}$ for all the experiments is $29.4_1$ kcal. per mole. The second law calculations indicate very little scatter within one experiment; however, there is appreciable diversity among the various experiments giving an average value of 29.55 ± 0.4 kcal. per mole. There is no indication that the tin manometer system gives results different from those with the bourdon gage. In Experiment 4, the sample size is approximately half that of the others which would increase the uncertainty in $K_p$. However, it is still in good agreement with the others.

The present work essentially confirms the previous work of Fischer, Ralhfs, and Benze (*3*) and Smits and Meijering (*5*). The third law values of $\Delta H_{d_{298}}$ agree with a precision of less than 0.1 kcal. per mole at the value 29.36 kcal. per mole. For the second law calculations, the average from the three authors is 29.66 ± 0.2 kcal. per mole which agrees with the third law value to within 0.3 to 0.4 kcal. per mole. These results show that the vapor density data for the dissociation of dimeric aluminum chloride are reliable and the free energy functions used in the third law calculations are sufficiently accurate to give a reasonable, consistent agreement with the second law value.

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