[CONTRIBUTION FROM THE ALUMINUM RESEARCH LABORATORIES]

Equilibrium and Rate of Aluminum Monochloride Formation from Aluminum Chloride and Aluminum[1]

BY ALLEN S. RUSSELL, KENNETH E. MARTIN AND C. NORMAN COCHRAN

Aluminum monochloride formation from aluminum chloride and aluminum has been measured by determining the amount of aluminum transported by aluminum chloride in an alumina-lined quartz vessel. The equilibrium corresponded to 13.4% reaction at 1115° and 74 cm. pressure. From the derived heat of aluminum monochloride formation at 0°K., −10.7 kcal., and other thermodynamic data, the equilibrium curves for monochloride formation have been drawn for a range of temperatures and pressures. Under the test conditions employed, the reaction rate was largely controlled by the diffusion of aluminum chloride to the aluminum surface against the stream of monochloride diffusing away from it.

Introduction

Aluminum halides cause aluminum to volatilize at temperatures where its vapor pressure is negligible and to redeposit as metal when cooled. Aluminum monochloride[2] has been proved spectroscopically to be involved in the chloride distillation. The reaction

$$AlCl_3 + 2Al \longrightarrow 3AlCl \qquad (1)$$

has been investigated by measuring the amount of aluminum transported when aluminum chloride was passed over heated aluminum in an alumina-lined quartz tube. For ease of interpretation, the rate experiments had to be conducted at pressures where the reaction can be essentially complete for a range of temperatures. Inasmuch as it was more convenient to measure the reaction equilibrium at atmospheric pressure, two sets of experiments (atmospheric and low pressure) have been conducted. The effect of an electrical discharge has also been examined.

NOTE ADDED IN PROOF.—P. Weiss (*Z. Erzbergbau u. Metallhuttenwesen*, **3**, no. 8, 241 (1950)) has reported experiments of this same type which however indicate a much greater fraction aluminum chloride reacting than is shown by our data. The reason for this discrepancy is not evident. Our values agree, in general, with the published results[8,9] and privately communicated data of Gross as well as with results of larger scale experimentation in our laboratories.

Experimental

The apparatus used for atmospheric pressure tests is shown in Fig. 1.

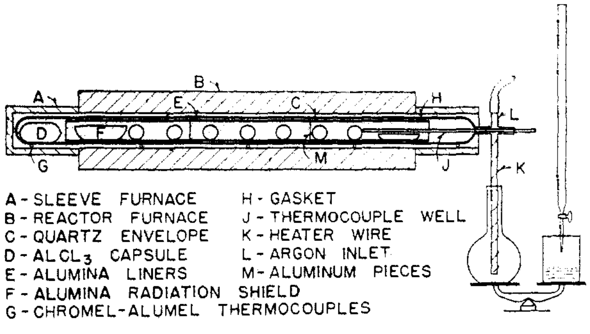

Fig. 1.—Apparatus.

The aluminum had a purity of 99.98%. The aluminum chloride was distilled in a separate Pyrex glass apparatus, condensed and sealed off as a capsule in the vacuum of a Cenco Hyvac pump. This capsule broke to free the chloride on subsequent heating at about 125° where the chloride vapor pressure was still low.

The reaction vessel consisted of a 58"-long, 1" o.d. quartz tube sheathed internally with three alumina liners. The aluminum chloride capsule was inserted to the closed end of the quartz tube and then the alumina liners containing the aluminum and radiation shields were placed closely together in the high temperature zone. The last liner was secured tightly against the quartz envelope in the low temperature exit end of the system by an aluminum foil gasket.

After the unit was assembled, a 12" length of 8 mm. o.d. quartz with two side-arms was joined axially to the main quartz tube. An alumina-sheathed quartz thermocouple well, which was inserted into the main quartz tube until it nearly touched the last aluminum piece, was sealed to the 8-mm. quartz by deKhotinsky cement. One of the side-arms served as an inlet for argon, and the other led into a 2-liter Pyrex flask in which chloride was condensed and weighed during the run. Temperatures were measured by a series of chromel-alumel thermocouples calibrated at the fusion point of sodium fluoride 991°.

For a run, the apparatus was evacuated by a Cenco Hyvac pump and the reactor was heated until it was constant at the desired temperature. The vacuum was broken with argon, which was kept passing through the exit tube to prevent an inflow of air. The sleeve furnace over the aluminum chloride was heated rapidly until the capsule broke. A constant aluminum chloride flow rate was maintained for one hour, after which the entire apparatus was cooled rapidly, the quartz tube was dismantled and the components were examined and weighed.

The equipment for low pressure was generally like that for atmospheric pressure except a shorter reaction zone and fewer aluminum pieces were used. At the exit end of the quartz tube a bulb for collecting the aluminum chloride was inserted before the vacuum pump. The aluminum chloride flow rate was maintained by following a temperature schedule established in earlier blank runs.

Preliminary vacuum runs showed that a manometer sealed onto the quartz tube where aluminum chloride entered the hot zone gave an accurate reading of aluminum chloride pressure at the first aluminum particle. Silicone 200 fluid, which was maintained near 200°, was used in the manometer.

To investigate the effect of an electrical discharge on the reaction, the low pressure apparatus was modified by sealing a short piece of capillary tubing to the closed end and a side-arm to the exit end of the main quartz tube. Electrical leads were sealed through these tubes with de Khotinsky cement. One was attached to a strip of graphite supporting the aluminum pieces in the alumina-lined reaction zone. The other was attached to an aluminum foil liner in the exit end of the system.

Calculation of Equilibrium

General Theory.—Aluminum chloride vapors would be expected to react at constant temperature with successive particles of aluminum until the aluminum monochloride concentration increased to a definite value dependent on the pressure and temperature. The aluminum chloride reacting could then be calculated from the weight of aluminum chloride passed and the weight of aluminum lost from an infinite number of particles,

Per cent. aluminum chloride reacting = (100 × g. aluminum wt. loss)/(54/133 × g. aluminum chloride passed)

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(1) Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, September, 1950.

(2) L. M. Foster, Allen S. Russell and C. Norman Cochran, THIS JOURNAL, **72**, 2580 (1950).

where the fraction 54/133 comes from the stoichiometric weights in equation (1). An accurate value of the aluminum chloride reacting at a known pressure and temperature, in conjunction with other thermodynamic data, permits calculation of the equilibrium over a range of pressures and temperatures.

Equilibrium from Weight Loss.—When aluminum chloride was passed over a series of aluminum particles at approximately constant temperature, the major weight loss occurred from the first few particles. However, each particle lost weight even when a succession of thirty was employed. Some aluminum was deposited on the alumina liners of the reaction zone adjacent to particles from which distillation occurred. The net aluminum transported was obtained by subtracting from the total particle weight loss the amount of aluminum deposited on the liners in the reaction zone. This value was used to calculate the equilibrium per cent. of aluminum chloride reacting.

Equilibrium from Condensation Temperature.—Equilibrium can be judged from the temperature of aluminum condensation even though the reaction zone is not at constant temperature nor of great extent. After the run, the point of first aluminum deposition on the thermocouple sheath is noted and related to temperature by a previous calibration. The equilibrium gas composition at the temperature of first deposition is known from the weight of aluminum and aluminum chloride transported.

There is some experimental error in this procedure. The most serious question is whether aluminum deposition starts at the equilibrium point or whether a supersaturation of vapor occurs. The second most troublesome problem is the determination of the exact point of aluminum laydown.

In view of the lack of complete equilibrium on reaction and the possible supersaturation of aluminum monochloride on condensation, some attention should be paid to both values in determining the true equilibrium.

Equilibrium

At One Atmosphere Aluminum Chloride Pressure.—Table I shows the results of nine experiments in which aluminum chloride was passed at one atmosphere pressure over a long series of aluminum particles at 1125°. The average value of aluminum chloride reacting was 13.4%.

The per cent. of aluminum chloride reacting was calculated from the aluminum chloride passed and the net aluminum transported. The weight of aluminum condensed does not include the aluminum deposited in the immediate vicinity of the charge particles. Some aluminum was always carried through its condensing zone by aluminum chloride so that the weight of aluminum condensed was somewhat less than the net aluminum transported from the aluminum particles. Usually about 0.2 to 0.4 g. of aluminum was found by chemical analysis in the aluminum chloride in runs like those in Table I at 1125°.

TABLE I

ATMOSPHERIC PRESSURE DISTILLATION OF ALUMINUM WITH ALUMINUM CHLORIDE, REACTION ZONE TEMPERATURE 1125°

Run	Charge wt., g.	$AlCl_3$ passed, g.	Al wt. loss, g.	Al condensed, g.	Net Al transported, g.	$AlCl_3$ reacting, %
1	6.7	36	2.07	..	1.95	13.4
2	6.8	28	1.67	1.13	1.55	13.6
3	7.0	27	1.53	1.12	1.38	12.6
4	6.4	49	3.18	2.47	3.04	15.2
5[e]	6.4	32	1.76	1.36	1.76	13.8
6[e]	6.1	21	..	..	1.10	13.0
7	16.0	30	2.07	..	1.35	11.1
8[f]	12.7	20[a]	1.58	0.81	1.12	13.9
9[f]	12.7	24[a]	1.78	..	1.34	13.8
10[b]	6.5	14[d]	3.83	0.65	1.10	20.2
11[b]	13.8	30	8.33	1.80	2.27	18.6
12[c]	12.8	32	8.12	0.61	1.64	12.6

[a] Forty-minute runs. [b] Hydrogen chloride. [c] Chlorine. [d] Thirty-minute run. [e] System extremely dry. [f] Condensation temperature 1105°.

At the junction of each of the liners, aluminum monochloride escaped to react with the surrounding quartz tube and remove monochloride from the vapor stream. This, of course, permitted additional chloride to react with aluminum to supply the loss. Also some aluminum chloride passed between the alumina liners and the quartz envelope until it was forced by the seal to pass through the last liner. The 1125° heating changed the thermocouple calibration, and it was difficult to obtain both radial and axial uniformity. In the two atmospheric pressure runs where the condensation temperature of aluminum was noted, the value was 1105° when the reaction temperature was 1125°. It is assumed that equilibrium was complete at the average of these two values, namely, 1115°.

Effect of Water.—In two experiments, the distillation has been run as nearly as possible in the absence of water or hydrogen chloride. In these "dry runs," the predistillation unit was evacuated by a mercury diffusion pump using a trap cooled with Dry Ice–acetone. The aluminum chloride was doubly distilled with all precautions. The apparatus was evacuated with the reaction zone temperature at 1125°, the aluminum chloride portion at 50° and the balance of the system above 300°. The aluminum chloride capsule was free of alumina after the runs, showing that water had not been present in appreciable concentration. The per cent. of aluminum chloride reacting agreed with regular runs.

Distillation with Hydrogen Chloride and Chlorine.—Table I shows results of runs employing hydrogen chloride and chlorine for the distilling medium. These gases were dried by passage through a trap cooled to Dry Ice temperature before they entered the reaction zone. Although the large subtraction from total weight loss for aluminum chloride production makes the final results of low accuracy, the general conclusions are the same as for regular runs.

At Low Aluminum Chloride Pressure.—The measured equilibria in these low pressure runs are compared in Table II with thermodynamic extrapolations based on the atmospheric pressure data. The measured condensation temperatures agree satisfactorily in most cases, but are uniformly lower than those from the atmospheric pressure extrapolation.

TABLE II

LOW PRESSURE DISTILLATIONS OF ALUMINUM WITH ALUMINUM CHLORIDE

Cenco Hyvac pump vacuum: pressure read on manometer containing Silicone DC200 fluid.

Run	Reaction zone temp., °C.	Run duration, hr.	$AlCl_3$ passed, g.	$AlCl_3$ pressure, cm.	Al wt. loss, g.	Al condensed, g.	$AlCl_3$ flow rate, g./hr.	Condensation temp., °C. Measd.	Condensation temp., °C. Calcd.	$AlCl_3$ reacting, %
13	950	2.00	2.8	0.05	1.1	1.0	1.4	840	...	100
14	950	1.00	2.8	.05	0.9	0.8	2.8	...	...	82
15	950	1.00	3.9	.05	1.3	1.2	3.9	780	830	81
16	950	1.00	5.7	..	1.6	1.6	5.7	...	...	70
17[b]	950	3.48	22.4	.05	6.2	6.2	6.6	760	...	>68
18	950	1.00	7.4	.05	2.2	2.1	7.4	...	...	73
19	950	1.00	9.0	..	2.3	2.3	9.0	...	...	64
20	1000	1.00	9.3	..	2.5	2.5	9.3	...	...	66
21	950	0.87	21.3	.22	4.6	4.4	24.4	850	860	54
22	1050	0.50	20.9	.28	4.5	4.3	40.4	840	870	53
23[c]	1050	0.50	23.0	.22	4.0	3.7[a]	46.0	840	850	43
24	950	0.50	23.8	.22	3.0	2.9	47.5	740	820	31
25	900	0.50	35.1	.18	3.0	2.8[a]	70.2	790	790	21

[a] Aluminum condensed on thermocouple shield was not weighed. [b] All aluminum consumed. [c] Aluminum pieces flowed together.

Rate

Either of two steps may control the rate of this reaction; the one involving a slow sorption, desorption or reaction on the surface of the aluminum particle, and the second being diffusion of aluminum chloride to the aluminum surface against the stream of monochloride diffusing away from it. The experimental criterion for distinguishing these is that the first would have a high and the second a low temperature coefficient under conditions such that equilibrium would correspond to nearly complete reaction for all of the runs.

Extrapolation of the weight loss per particle data in runs of low aluminum chloride flow rate showed that nearly complete reaction would have been attained if a sufficient number of particles had been used. This result indicates that experimental conditions were satisfactory for determining the factor governing the rate of reaction. Equilibrium data were obtained by measurement of the metal condensation temperatures.

The per cent. of aluminum chloride reacting in the low pressure runs is shown in Fig. 2 to be strongly dependent on the aluminum chloride flow rate. In addition, the amount reacting is shown to be nearly independent of temperature under these conditions. This latter finding indicates that the rate of this reaction is governed to a large degree by a diffusion mechanism for our test conditions.

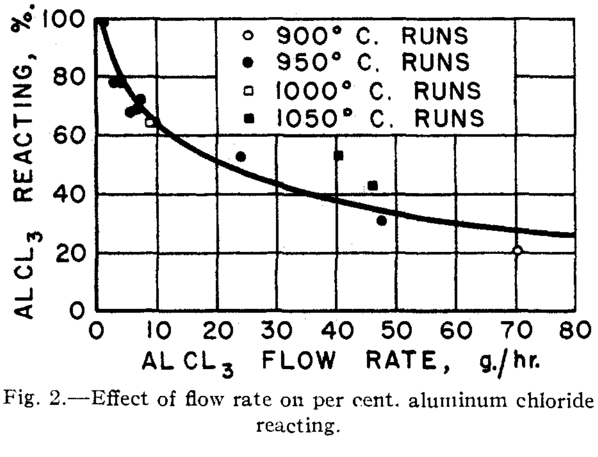

Fig. 2.—Effect of flow rate on per cent. aluminum chloride reacting.

Electrical Discharge

The effect of an electrical discharge on the distillation of aluminum with aluminum chloride was examined in experiments at 950° under Cenco Hyvac pump vacuum. There was no attempt to determine the pressure, but it was probably less than 0.1 cm. of mercury. The generator supplied 4000 volts d. c. at 20 milliamperes (half-wave rectified). Our vacuum apparatus was in the earliest stages of development so that reproducibility of these runs was quite low. However, there was no marked effect of an electrical discharge on equilibrium or rate of reaction when the polarity of the aluminum pieces was either positive or negative.

Aluminum Monochloride Energy of Formation

The best value of the fraction aluminum chloride reacting (α) to form monochloride is 0.134 at a temperature of 1115° and a total pressure (P) of 74 cm. This is equivalent to 0.132 at 76 cm. of mercury and 1115°, or 0.145 at 1127° (1400°K.) and 76 cm. The equilibrium constant (K) for reaction (1) at 1400° K. and one atmosphere total pressure is then

$$K = 27\alpha^3P^2/(1 - \alpha)(1 + 2\alpha)^2 = 0.0579 \qquad (2)$$

From this, $\log K = -1.238$ and hence the standard free energy change (ΔF°) of the reaction at 1400° K. is

$$-\Delta F^\circ/T = 4.57 \log K = -5.66 \qquad (3)$$

Combining this with free energy functions $[(-F^\circ/T)$ calculated for aluminum as 11.85[3,4] and for aluminum chloride[5,6,7] as 183.23 at 1400° K. we find the free energy function of aluminum monochloride.

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(3) K. K. Kelley, Bulletin 476, U. S. Department of Interior, Bureau of Mines 1949.

(4) W. F. Giauque and P. F. Meads, THIS JOURNAL, **63**, 1897 (1941).

(5) W. D. Treadwell and L. Terebesi, *Helv. Chim. Acta*, **18**, 103–120 (1935).

(6) A. Smits and J. L. Meijering, *Z. physik. Chem.*, **B41**, 98–111 (1938).

(7) Selected Values of Chemical Thermodynamic Properties, Series III, $Cl_2(g)$, National Bureau of Standards.

$$\frac{(F^0)}{(T)_{\mathrm{AlCl}}} = \frac{1}{3}\left[\frac{(\Delta F^0)}{(T)} + \frac{(F^0)}{(T)_{\mathrm{AlCl_3}}} + 2\,\frac{(F^0)}{(T)_{\mathrm{Al}}}\right] = -67.09 \quad (4)$$

Then with the function $-(F^0 - E_0^0)/(T)_{\mathrm{AlCl}} = 59.45$[2] we have

$$E_0^0/T = -7.64 \text{ or } E_0^0 = -10.7 \text{ kcal.} \quad (5)$$

E_0^0 represents the energy necessary to form aluminum monochloride with all materials in their standard states at 0° K. by the reaction

$$\mathrm{Al(s)} + {}^1/_2\mathrm{Cl_2(v)} \longrightarrow \mathrm{AlCl(v)} \quad (6)$$

Our value is to be compared with the recent determination by Gross[8,9] of -11.6 kcal. for the ΔH^0 of the reaction at 25°, which to this accuracy equals E_0^0.

Since all the thermodynamic values other than this E_0^0 had already been known, the entire equilibrium picture for this reaction can be constructed. Values for the logarithm of the equilibrium constant as a function of temperature are given in Fig. 3. The temperature necessary for a given fraction of aluminum chloride reacting with aluminum to form aluminum monochloride is shown as a function of total pressure in Fig. 4.

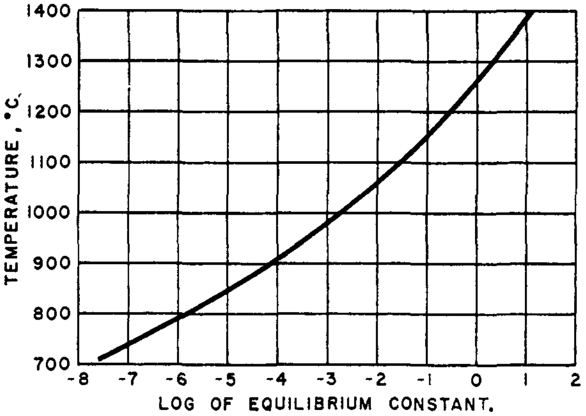

Fig. 3.—Effect of temperature on equilibrium constant for the reaction $\mathrm{AlCl_3} + 2\mathrm{Al} \rightarrow 3\mathrm{AlCl}$.

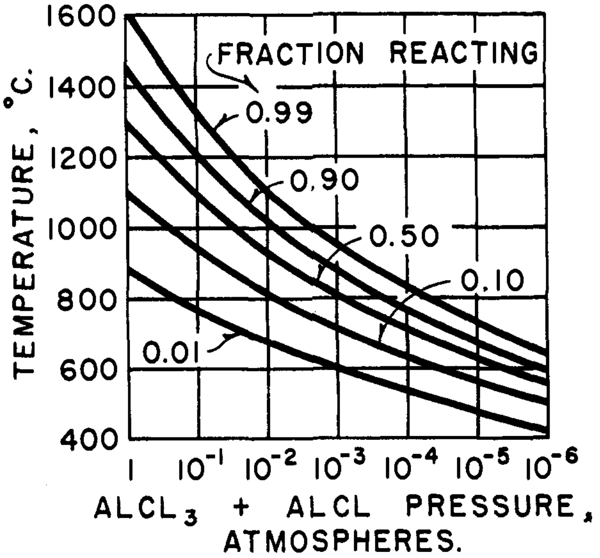

Fig. 4.—Temperature necessary for a given fraction of aluminum chloride reacting with aluminum to form aluminum monochloride as a function of pressure.

NEW KENSINGTON, PA.

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(8) P. Gross, C. S. Campbell, P. J. C. Kent and D. L. Levi, *Discussions Faraday Soc.*, **4**, 206 (1948).

(9) P. Gross, "The Refining of Non-Ferrous Metals, Institution of Mining and Metallurgy," London, 1950, p. 461.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS AND FROM THE CHEMISTRY LABORATORY OF NORTHWESTERN UNIVERSITY]

Studies on the Oxidation of Potassium Ruthenocyanide[1,2]

BY DONALD D. DEFORD AND ARTHUR W. DAVIDSON

Titrimetric, spectrophotometric and polarographic data indicate that the ruthenocyanide ion is oxidized to ruthenicyanide ion upon treatment with strong oxidizing agents. The chemical behavior of the ruthenicyanide ion in solution is described. The standard potential of the ruthenocyanide–ruthenicyanide couple is estimated to be -0.86 ± 0.05 volt. Attempted preparation of crystalline potassium ruthenicyanide has been unsuccessful.

Potassium ruthenocyanide, $\mathrm{K_4Ru(CN)_6}$, was first prepared by Claus[3] almost one hundred years ago. The properties of this compound, and of other ruthenocyanides and their derivatives, have been studied by a number of investigators[4] since that time. From the position of ruthenium in the periodic table, one would expect to find a close similarity between potassium ruthenocyanide and potassium ferrocyanide. The work of previous investigators has verified this expectation. In spite of the fact that these similarities have been known for many years, no previous investigation has been undertaken to determine whether ruthenocyanide ion can be oxidized to ruthenicyanide, $\mathrm{Ru(CN)_6^{\equiv}}$, under conditions similar to those under which ferrocyanide is oxidized to ferricyanide. The present

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(2) Presented at the Symposium on the Less Familiar Elements at the Detroit Meeting of the American Chemical Society, April, 1950.

(3) C. Claus, "Beitrage zur Chemie der Platinmetalle," Dorpat, 1854, p. 97.

(4) (a) G. A. Barbieri, *Atti accad. nazl. Lincei*, [6] **9**, 1015 (1929); (b) A. K. Bhattacharya, *J. Indian Chem. Soc.*, **13**, 284 (1936); (c) D. M. Bose, *Indian J. Physics*, **9**, 277 (1934–1935); (d) H. Dufet, *Compt. rend.*, **120**, 377 (1895); (e) J. L. Howe, THIS JOURNAL, **18**, 981 (1896); (f) J. L. Howe and E. D. Campbell, *ibid.*, **20**, 29 (1898); (g) F. Krauss and G. Schrader, *Z. anorg. Chem.*, **165**, 59 (1927); (h) F. Krauss and G. Schrader, *ibid.*, **173**, 63 (1928); (i) W. Manchot and J. Dusing, *ibid.*, **212**, 109 (1933); (j) W. Manchot and J. Dusing, *Ber.*, **63**, 1226 (1930); (k) R. Samuel and A. R. R. Despande, *Z. Physik*, **80**, 395 (1933); (m) R. Samuel and M. J. Khan, *ibid.*, **84**, 87 (1933).