

The Apparent Solubility of Aluminum in Cryolite Melts

K. YOSHIDA AND E. W. DEWING

The apparent solubility of aluminum in cryolite melts saturated with Al_2O_3 has been determined by titration with electrolytically generated O_2 . The results may be expressed by

$$\begin{aligned} \text{wt pct Al} = & -0.2877 + 0.0268 (\text{NaF}/\text{AlF}_3 \text{ wt ratio}) \\ & + 2.992 \times 10^{-4} (\text{temp } ^\circ\text{C}) - 0.00192 (\% \text{CaF}_2) \\ & - 0.00174 (\% \text{Li}_3\text{AlF}_6) - 0.00288 (\% \text{NaCl}) \end{aligned}$$

with a standard deviation of ± 0.017 . Ranges covered were ratio 0.8 to 2.3, temperatures 969° to 1054°C , $\text{CaF}_2 \leq 14$ pct, $\text{Li}_3\text{AlF}_6 \leq 20$ pct, and $\text{NaCl} \leq 10$ pct. There was no significant effect of adding 0 to 38 pct K_3AlF_6 or 0 to 10 pct MgF_2 . It was found that solubility was approximately proportional to activity of aluminum when Al-Cu alloys were used. Possible mechanisms of solution are discussed. Monovalent aluminum is ruled out on the basis of the variation of solubility with NaF/AlF_3 ratio and a_{Al} . The favored, but not proven, mechanism involves formation of both sodium atoms and a colloidal dispersion of aluminum.

IT is well established that the chief cause of loss of current efficiency in aluminum electrolysis is dissolution of aluminum in the electrolyte and subsequent re-oxidation by CO_2 in the anode gas. (For present purposes the word "solution" is taken to include colloidal dispersions or "fogs.") Several measurements of the solubility of aluminum in cryolite have been made recently,¹⁻⁴ but since the results vary by a factor of twenty it was apparent that more work was required. The results are very dependent on the experimental method used. Gerlach, Schmidt, and Schmidt³ and Yoshida, Ishihara, and Yokoi,⁴ measured the loss of weight of aluminum in cryolite and assumed that the loss represented metal in solution; they obtained solubilities of the order of 1 pct. Thonstad² and Haupin¹ made determinations of hydrogen evolved from the frozen cryolite and obtained values of the order of 0.1 pct. The former method can give high results due to reaction of the aluminum with the crucible material or escape of vapor from the crucible; the latter suffers from uncertainties arising from possible oxidation of precipitated metal during handling of the samples, and if aluminum carbide is present some of the gas evolved will be methane and not hydrogen. To avoid some of these uncertainties it was decided to make analyses on the hot melts without freezing them or withdrawing them from the crucible, and titration with electrolytically generated oxygen seemed the most promising method. The alternative, coulometric determination by direct anodic oxidation, did not give reproducible results. Mass transfer was sufficiently slow that excessively long times were required for complete oxidation. With the oxygen generation method the evolved gas bubbles had a large surface area and generated turbulence, and reaction was rapid.

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EXPERIMENTAL

The apparatus is shown in Fig. 1. The melt to be analyzed was isolated in the central 10 mm ID alumina tube. To prevent bulk metallic aluminum from entering this tube its bottom rested inside an alumina crucible 19 mm ID by 33 mm high. The whole melt was contained in another alumina crucible 46 mm ID by 72 mm high which served to prevent formation of Al_4C_3 by reaction of aluminum with the outer graphite crucible. Since Al_4C_3 is soluble in cryolite⁵ and is oxidizable by oxygen this is necessary. The melt had to be saturated with alumina in order to prevent attack on the alumina crucibles, but even so it soaked through them quite rapidly and the outer graphite crucible was

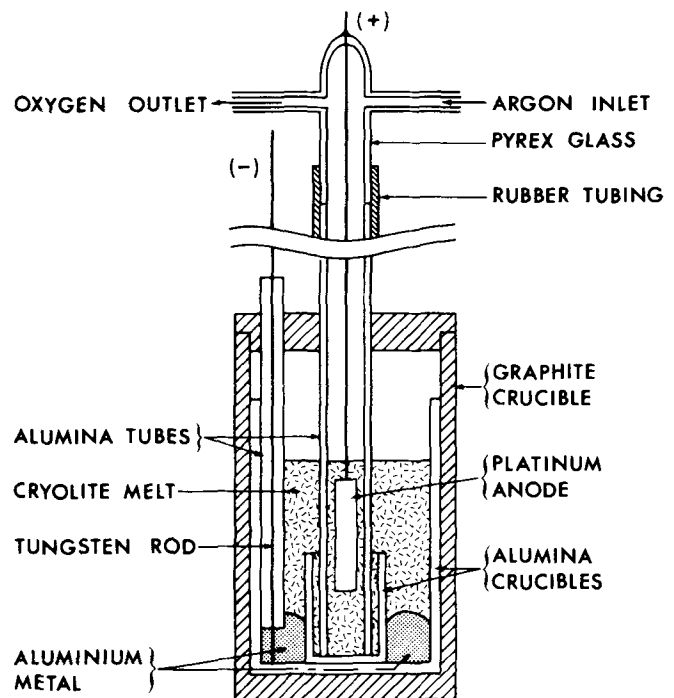


Fig. 1—Apparatus.

essential to prevent it escaping. The electrical resistance of the central alumina tube became low enough that there was no problem in passing current through it.

The whole apparatus was contained in an Inconel tube, insulated on top with refractory bricks, and flushed with argon. Temperatures were measured with a Pt-10 pct Rh thermocouple located outside the graphite crucible.

The cylindrical platinum anode was made from sheet 30 by 40 by 0.08 mm, and it was normally located 2 cm from the bottom of the tube. This position was a compromise. If it was placed much lower there was evidence that oxygen was escaping from the bottom of the tube; if it was placed much higher lower values were obtained for the content of dissolved metal, presumably because the gas bubbles were no longer reaching the bottom and some metal was remaining unoxidized. This is discussed further below. The top of the central tube was connected to a glass system in which the evolved oxygen could be collected over water. The volume of the glass tubes was kept small in order to minimize blanks.

A constant direct current was obtained from a Harrison 6200B power supply, and was measured by determining the potential drop across a suitable resistor.

The cryolite used was hand-picked natural material from Greenland, the alumina was a low-soda type (Alcan C-75), aluminum fluoride was distilled at high temperature, and other materials were reagent grade.

When the electrolyte was melted, a tungsten rod was inserted into the central tube to measure the depth of the melt. After this measurement the glass part was attached to the top and argon was let in to push the surface of the melt inside the tube down to the bottom. Bubbling was avoided since dissolved aluminum has a high vapor pressure and is easily lost from the melt. The system was kept for at least 1.5 hr after melting to allow equilibrium to be reached.

To start a run the argon inlet was closed and oxygen outlet was opened so that the melt came up into the alumina tube. Then the current, usually 1.006 A, was started. If unusually large quantities of dissolved metal were present a higher current was necessary or generation of oxygen was insufficiently fast to prevent the pressure in the tube dropping below atmospheric as reaction took place; this sucked fresh melt in from outside bringing with it more dissolved metal and leading to erroneous results. Readings of gas volume were made at intervals of about 1 min for 8 to 9 min.

After a run the current was stopped, the oxygen outlet was closed, and argon was let in to push out the melt in the alumina tube. Then the system was kept for about 20 min to be saturated again. At the end of a series of runs the depth of melt was remeasured, and samples were taken for analysis for NaF/AlF₃ ratio and the content of any additives.

In some cases the electromotive force between the electrodes was measured. Normally values around 2.1 to 2.2 v were found, indicating that oxygen was indeed being evolved, but occasionally much lower values were encountered. These indicated that carbon dust had got into the central compartment, and results from such runs were rejected.

All the usual corrections for vapor pressure of water, and so forth, were applied to the measured gas volumes.

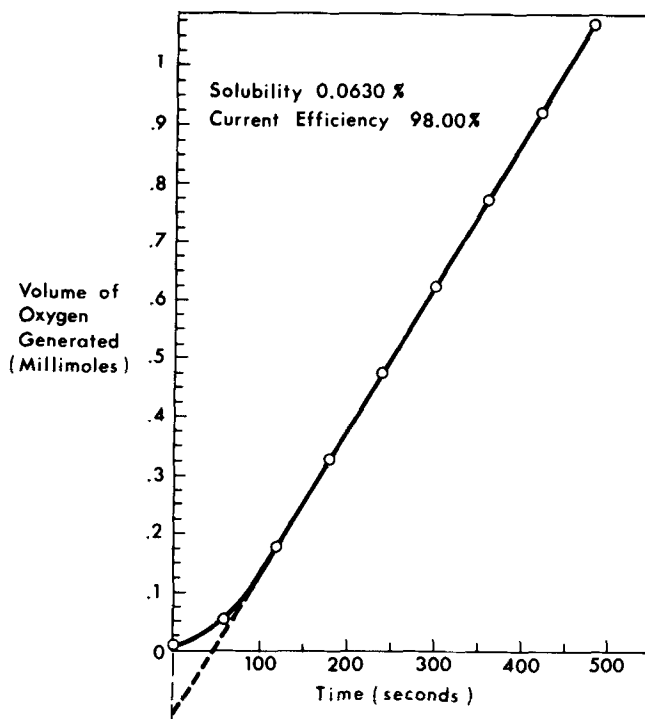


Fig. 2—Volume of oxygen generated as a function of time after starting the current.

RESULTS

Fig. 2 shows the results obtained from a typical run. After the first two min the volume of oxygen generated became a linear function of time, and extrapolation back to zero time gave the amount of oxygen consumed by the dissolved aluminum present. The latter was calculated as wt pct Al with densities of the melts derived from the literature.⁶⁻¹⁰ The current efficiency after the dissolved aluminum was destroyed was derived from the slope of the straight line. Experiments with aqueous CuSO₄ solution gave an apparent current efficiency of 97.42 ± 0.47 (standard error) pct. The discrepancy was assumed to lie in the gas measurement system, and a correction was made to all results with cryolite. The validity of the correction was confirmed by leaving some samples in the inner tube for 10 to 20 min after the end of a run, and then restarting the current as if it were a new run. The efficiencies thus found were 100.1 ± 2.4 (standard deviation) pct, and the intercepts on these blank samples corresponded to 0.0012 ± 0.0020 wt pct Al.

Fig. 3 shows the approach to equilibrium in two separate runs. For times longer than 1.5 h the values within any one run have become substantially constant.

Table I shows the results. A total of 270 measurements were made but those obtained successively in any one run have been averaged.

An initial regression analysis was carried out to express log (solubility) as a function of 1/T (in K), ratio, percentage of additives, and the height of the anode. In this way it was found that results with the anode 3 cm above the bottom needed to be multiplied by 1.40 to bring them into line with those obtained 2 cm above the bottom, which is regarded as the optimum position. This correction has been applied subsequently. The final regression analysis was done in a linear form so that solubility in wt pct Al was ex-

pressed as a function of temperature, ratio, and amounts of additives. The equation generated was:

$$S = -0.2877 + 0.0268 (\text{ratio}) + 2.992 \times 10^{-4} (\text{temp. } ^\circ\text{C}) \\ - 0.00192 (\% \text{ CaF}_2) - 0.00174 (\% \text{ Li}_3\text{AlF}_6) \\ - 0.00288 (\% \text{ NaCl})$$

This equation has a standard deviation of ± 0.017 wt pct Al, and gives a solubility of 0.052 wt pct at 1000°C with a NaF/AlF₃ wt ratio of 1.5 and no additives. The ranges covered were ratio 0.8 to 2.3, temperature 969° to 1054°C, CaF₂ up to 14 pct, Li₃AlF₆ up to 20 pct and NaCl up to 10 pct. There was no significant variation of solubility with K₃AlF₆ content in the range 0 to 38 pct, or MgF₂ content up to 10 pct. It will be realized that this equation applies to melts saturated with alumina.

DISCUSSION

It has been assumed implicitly in this work that the deficit of oxygen measured arose from reaction with dissolved metal. An alternative possibility would be that oxygen itself is soluble in cryolite. However, if this were the case, the measured solubilities would be independent of the activity of aluminum (see below) and would decrease with increasing temperature, both contrary to experience.

The chief uncertainty is the question of whether the melts were really saturated with dissolved metal. Unfortunately there is no way of being sure either one way or the other. An analysis of variance shows that the variation between runs was much higher than the variation within runs; this implies that the analytical method itself was reproducible and that the observed variation of metal content from one run to another was genuine. There would therefore appear to be some factor not under proper control. On the other hand, if one assumes that possible lack of saturation arises from loss of vapor (Na and AlF) from the surface of the melt, even in the extreme case where loss becomes so rapid that the surface concentration of dissolved metal drops to zero one would not expect the average concentration to be less than half saturated. This is because the area of aluminum exposed is approximately equal to the area of liquid in contact with the vapor, and the rate of dissolution should be rapid. In any case, it is hard to see that the concentration at the upper surface could drop to zero; the apparatus was fitted with a lid which, while not tightly sealed, must have severely restricted circulation of gas between inside and outside. It is noteworthy that Haupin,¹ working in a crucible without a lid, nonetheless found solubilities (by hydrogen evolution) of 0.1 wt pct Al at 980°C.

Figs. 4 and 5 show the results as a function of temperature and ratio. They are much lower than those obtained by measurements of loss of weight of aluminium,^{3,4} and are somewhat lower than those of Thonstad.² The variation with ratio is parallel to that found by Thonstad, but in the opposite direction to that found by Zhurin¹¹ and Mashovets and Svoboda.¹² Their measurements were made by gas evolution from samples equilibrated in graphite crucibles, without apparently any analysis of the gas. It is now known that

under those circumstances Al₄C₃ is dissolved in the melt and yields CH₄. Since the solubility of Al₄C₃ decreases as the ratio is raised⁵ it is most probable

Table I. Solubility of Aluminum in Cryolite Melts

Temp, °C	NaF/AlF ₃ Wt Ratio	Additive	Wt Pct	Solubility, Wt Pct Al	Note
1001	2.20	none		0.066	*
1003	1.46			0.034	*
1048	1.39			0.117	*
981	1.47			0.070	*
1000	1.38			0.064	*
980	1.33			0.051	*
1051	1.37			0.075	*
997	1.00			0.019	*
1002	1.25			0.057	*
997	1.53			0.043	*
999	0.80			0.028	*
1001	1.80			0.029	*
997	1.42			0.027	*
999	1.47			0.053	*
997	1.47			0.045	
1000	1.45			0.054	
1002	1.39			0.044	
999	1.43			0.085	
1052	1.38			0.043	
1051	1.32			0.049	
1002	1.44			0.030	
1000	1.47			0.041	
999	1.47			0.065	
1000	1.47			0.051	
1003	1.00			0.013	
1000	1.47	CaF ₂	4.5	0.028	
1001	1.46		4.5	0.064	
999	1.46		4.5	0.044	
999	1.49		9.0	0.046	
1000	1.45		9.0	0.014	
1002	1.48		9.0	0.036	
969	1.50		9.3	0.035	
1047	1.46		13.6	0.044	
1052	1.50		13.6	0.029	
1000	1.45	Li ₃ AlF ₆	17.2	0.023	
999	1.47		17.2	0.018	
1000	1.50		18.3	0.020	
1000	1.45		10.2	0.023	
998	1.45		10.1	0.043	
1000	1.49		9.5	0.033	
1000	1.43	K ₃ AlF ₆	15.7	0.031	
1001	1.42		15.6	0.033	
1001	1.42		16.3	0.027	
1001	1.36		8.6	0.074	
1001	1.47		8.6	0.062	
1000	1.43		8.3	0.061	
999	1.42		37.0	0.039	
1000	1.42		37.5	0.054	
999	1.41		36.8	0.055	
1000	1.50		16.9	0.070	
1000	1.50	NaCl	9.9	0.014	
999	1.50		9.8	0.014	
1000	1.50		4.9	0.021	
999	1.49		4.7	0.036	
1000	1.49		4.8	0.022	
999	1.48		9.7	0.016	
1000	1.50		14.0	0.024	
1000	1.49		14.0	0.027	
1000	1.47		3.0	0.062	
999	1.49		9.3	0.018	
1001	1.35	MgF ₂	9.3	0.047	
1001	1.36		9.4	0.069	
1001	1.37		9.6	0.054	

*These runs were made with the anode 3 cm above the bottom, and consequently the solubilities given have been multiplied by 1.40. See text.

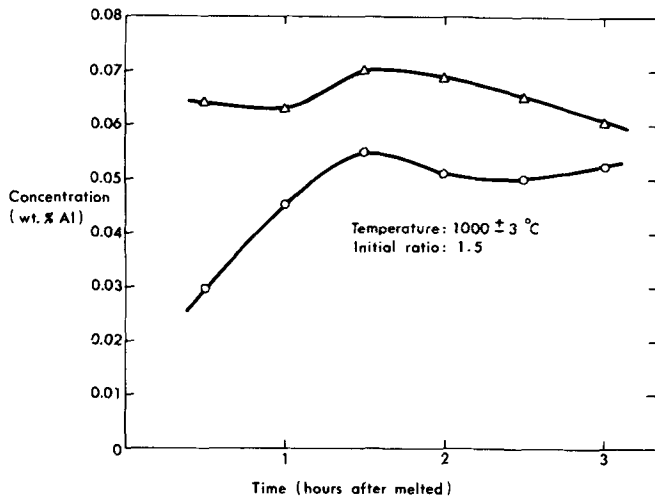


Fig. 3—Approach to equilibrium.

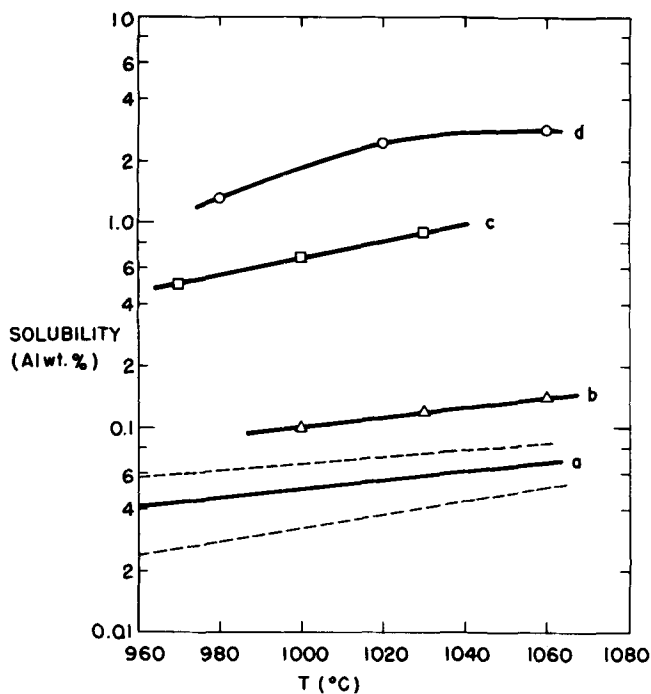
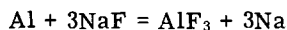


Fig. 4—Variation of solubility with temperature. (a) This work, (b) Thonstad,² (c) Gerlach *et al.*,³ (d) Yoshida *et al.*⁴

that this is what was being measured. In fact, if one takes the results of Mashovets and Svoboda and recalculates them in terms of Al_4C_3 they are close to the solubilities reported by Dewing.⁵ Fig. 6 shows the variation of solubility with activity of aluminum. Al-Cu alloys were used, and activity coefficients were taken from Wilder.¹³ The solubility seems to be proportional to activity within the rather low precision obtainable at such low metal concentrations. If the metal were dissolving as sodium, one would expect a slope of $\frac{1}{3}$ since the activity of sodium generated by the reaction



is proportional to $(a_{Al})^{1/3}$.

Both Haupin¹ and Thonstad² have found in their work with quenched samples that some of the hydrogen is evolved on reaction with water or alcohol, while the

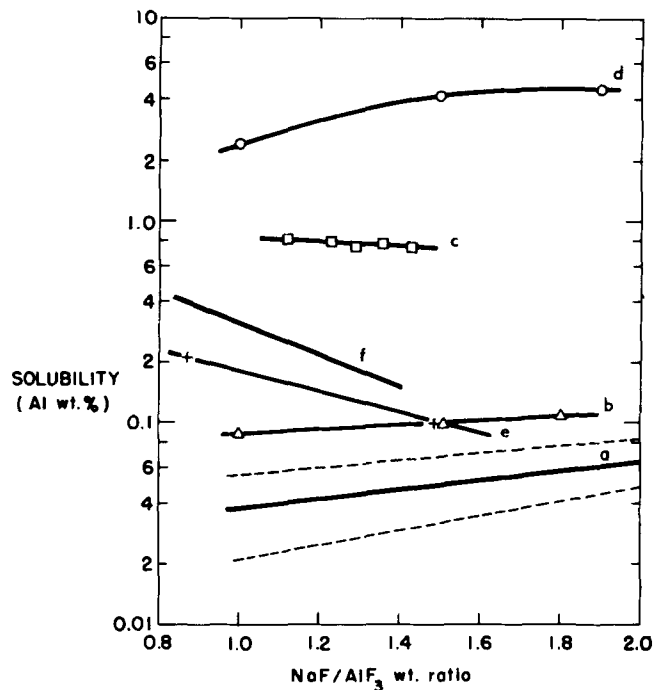


Fig. 5—Variation of solubility with NaF/AlF₃ ratio. (a) This work, (b) Thonstad,² (c) Gerlach *et al.*,³ (d) Yoshida *et al.*,⁴ (e) Zhurin,¹¹ (f) Mashovets and Svoboda.¹²

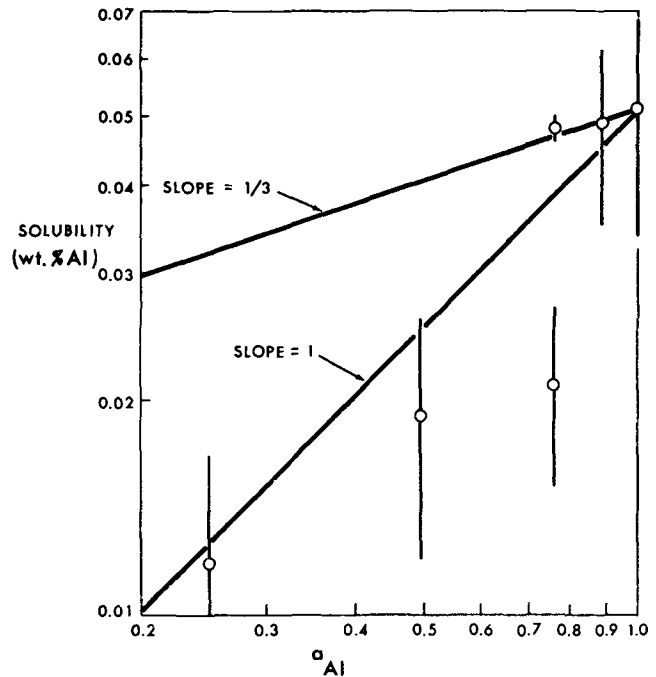


Fig. 6—Variation of solubility with activity of aluminum.

rest requires reaction with caustic soda or hydrochloric acid. They interpret the two reactions as corresponding to sodium and aluminum respectively. If this is correct, and if the quenching has preserved a state of affairs existing in the original melt, one would expect a plot of solubility against a_{Na} to give a straight line not passing through the origin. Activities are now available from concentration cell measurements,¹⁴ and Fig. 7 shows such a plot. The line representing the present results is derived from the regression equation above and is straight. Thonstad's results appear

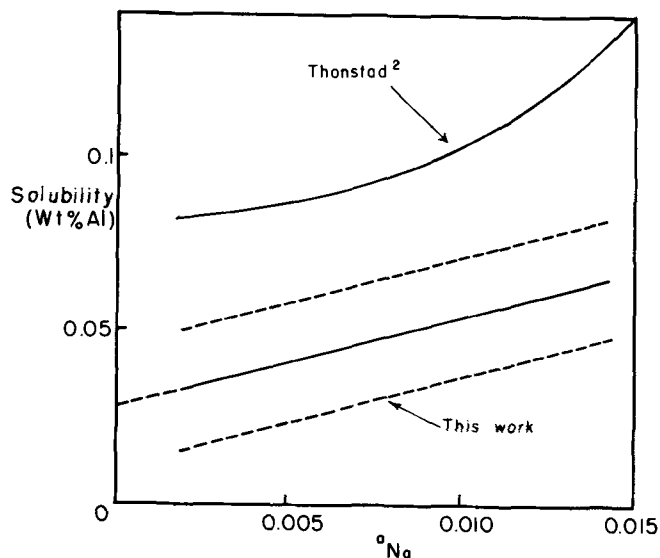


Fig. 7—Variation of solubility with activity of sodium.

to lie on a slight curve. Neither line passes through the origin. Qualitatively at least the results are consistent with the hypothesis, but difficulties arise. Firstly, if the solubility is partly as sodium, the line in Fig. 6 should not be as steep as it is. Secondly, what is the chemical form of the part supposed to be dissolved as aluminum? This question also arises if one accepts the evidence of Fig. 6, and assumes that all the dissolved metal is present as aluminum.

Solution as AlF or Al^+ can be ruled out. It would give a slope of $\frac{2}{3}$ in Fig. 6, and it would vary in the opposite direction with change in ratio. Solution as essentially inert aluminum atoms is also not possible—the solubility is of the order of 10^9 higher than would be expected on that basis.¹⁵

One possibility is that the part dissolved as aluminum is essentially colloidal. An analogous situation has been found by Richardson and Billington¹⁶ when copper dissolves in silicate melts—there is a genuine

solubility, but when the activity of copper is close to unity dispersions are formed. Reducing a_{Cu} to 0.7 or lower prevents them forming. In our case the data are not sufficiently precise to tell whether or not there is a sudden drop in solubility on first reducing the activity below unity, followed by a dependence on $(a_{Al})^{1/3}$. However, the hypothesis does have a number of attractions. It would be consistent with Fig. 7, it would account for the easy chemical distinction in quenched samples between metal reacting with water and that reacting only with HCl, and, since colloidal dispersions are inherently unreproducible, it might well account for the large scatter in the results.

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