

THE SOLUBILITY OF ALUMINUM IN CRYOLITE MELTS

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Abstract

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

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

with a standard deviation of + 0.017. Ranges covered were ratio 0.8 - 2.3, temperature 969 - 1054°C, $\text{CaF}_2 \leq 14\%$, $\text{Li}_3\text{AlF}_6 \leq 20\%$, and $\text{NaCl} \leq 10\%$. There was no significant effect of adding 0 - 38% K_3AlF_6 or 0 - 10% MgF_2 . It was found that solubility was approximately proportional to activity of Al when Al - Cu alloys were used.

Possible mechanisms of solution are discussed.

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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 reoxidation by CO_2 in the anode gas. 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 Schmidt⁽³⁾ 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%. Thonstad⁽²⁾ and Haupin⁽¹⁾ made determinations of hydrogen evolved from the frozen cryolite and obtained values of the order of 0.1%. The former method can give high results due to reaction of the aluminum with the crucible material or escape of vapour 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.

EXPERIMENTAL

The apparatus is shown in Figure 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 x 33 mm high. The whole melt was contained in another alumina crucible 46 mm ID x 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 cryolite⁽⁵⁾ 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 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 x 40 x 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 aluminium has a high vapour pressure and is easily lost from the melt. The system was kept for at least 1.5 hours 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 8-9 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 minutes 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 emf between the electrodes was measured. Normally, values around 2.1-2.2 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 vapour pressure of water, etc., were applied to the measured gas volumes.

RESULTS

Figure 2 shows the results obtained from a typical run. After the first two minutes 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 Al 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 (std. error) pct. The discrepancy was assumed to lie in the gas measurement system, and a correction was made to all results with cryolite. Checks on cryolite samples which had already been oxidized gave an efficiency of 100.1 ± 2.4 (std. devn.) pct, confirming the validity of the correction. The intercepts on these blank samples corresponded to 0.0012 ± 0.0020 wt pct Al.

A total of 270 measurements was made. 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 % Al was expressed 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 % Al, and gives a solubility of 0.052 wt % at 1000°C with a NaF/AlF₃ wt ratio of 1.5 and no additives. The ranges covered were ratio 0.8-2.3, temperature 969-1054°C, CaF₂ up to 14%, Li₃AlF₆ up to 20% and NaCl up to 10%. There was no significant variation of solubility with K₃AlF₆ content in the range 0-38%, or MgF₂ content up to 10%. It will be realized that this equation applies to melts saturated with alumina.

DISCUSSION

The chief uncertainty with this work 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 vapour (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 vapour, 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.

Figures 3 and 4 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 Zhurin⁽¹¹⁾ 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 Al_4C_3 is dissolved in the melt and yields CH_4 . Since the solubility of Al_4C_3 decreases as the ratio is raised⁽⁵⁾ it is most probable 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⁾. Figure 5 shows the variation of solubility with activity of Al. Al - Cu alloys were used, and activity coefficients were taken from Wilder⁽¹³⁾. It is apparent that solubility is proportional to activity within the rather low precision obtainable at such low metal concentrations. If the metal were dissolving as Na, one would expect a slope of 1/3.

Both Haupin⁽¹⁾ and Thonstad⁽²⁾ have found in their work with quenched samples that some of the hydrogen is evolved on reaction with water or alcohol, while the rest requires reaction with caustic soda or hydrochloric acid. They interpret the two reactions as corresponding to Na and Al 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 Figure 6 shows such a plot. The line representing the present results is derived from the regression equation above and is straight. Thonstad's results appear 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 Na, the line in Figure 5 should not be as steep as it is. Secondly, what is the chemical form of the part supposed to be dissolved as Al? This question also arises if one accepts the evidence of Figure 5, and assumes that all the dissolved metal is present as Al.

Solution as AlF or Al^+ can be ruled out. It would give a slope of 2/3 in Figure 5, and it would vary in the opposite direction with change in ratio. Solution as essentially inert Al 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 Al is essentially colloidal. An analogous situation has been found by Richardson and

Billington⁽¹⁶⁾ when Cu 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. However, the hypothesis does have a number of attractions. It would be consistent with Figure 6, 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.

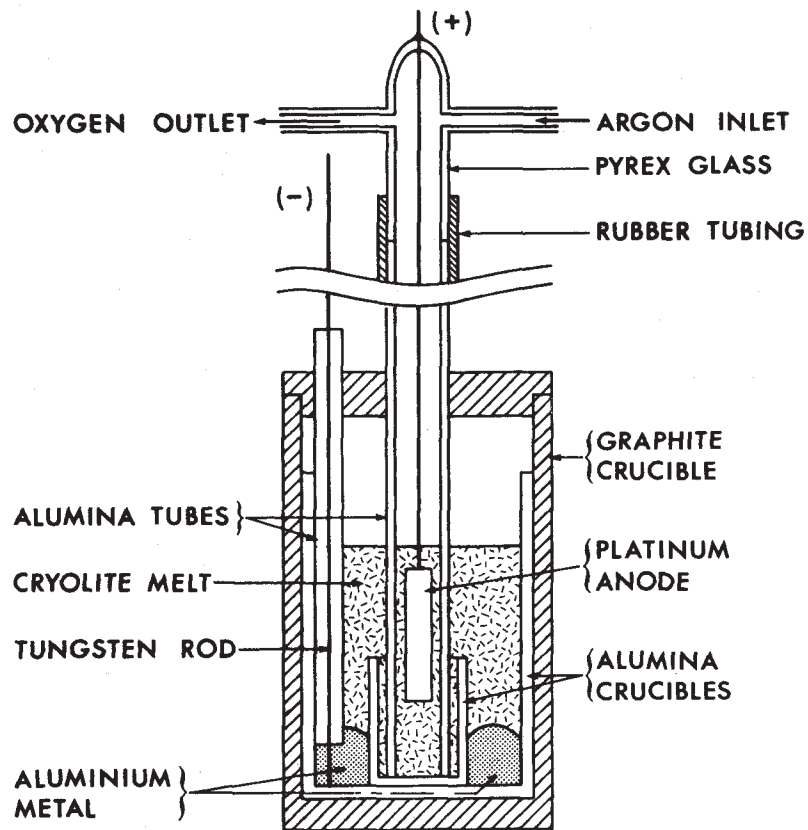


FIGURE: 1
APPARATUS

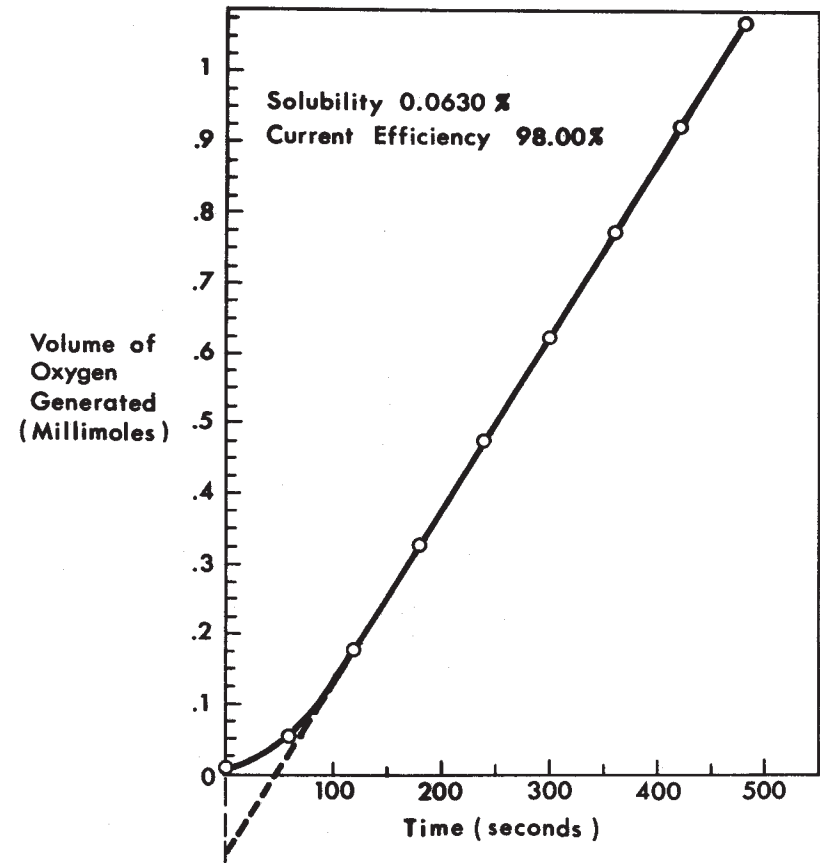


FIGURE: 2

Volume of oxygen generated as function of time after starting the current.

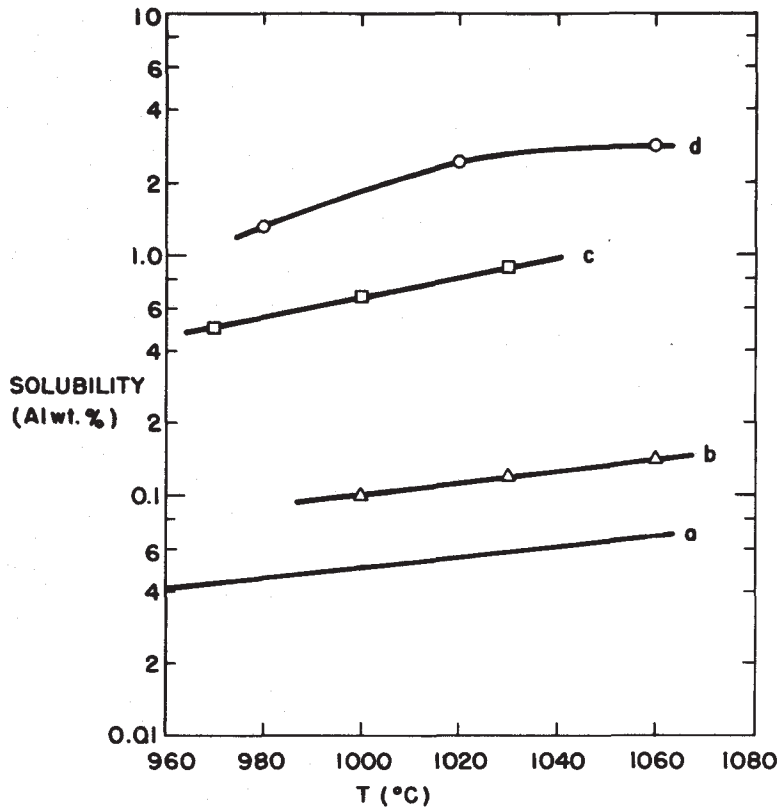


FIGURE 3

Variation of Solubility with Temperature.

- | | |
|----------------------------------|----------------------------------|
| a. This Work. | b. Thonstad ² . |
| c. Gerlach et al. ³ . | d. Yoshida et al. ⁴ . |

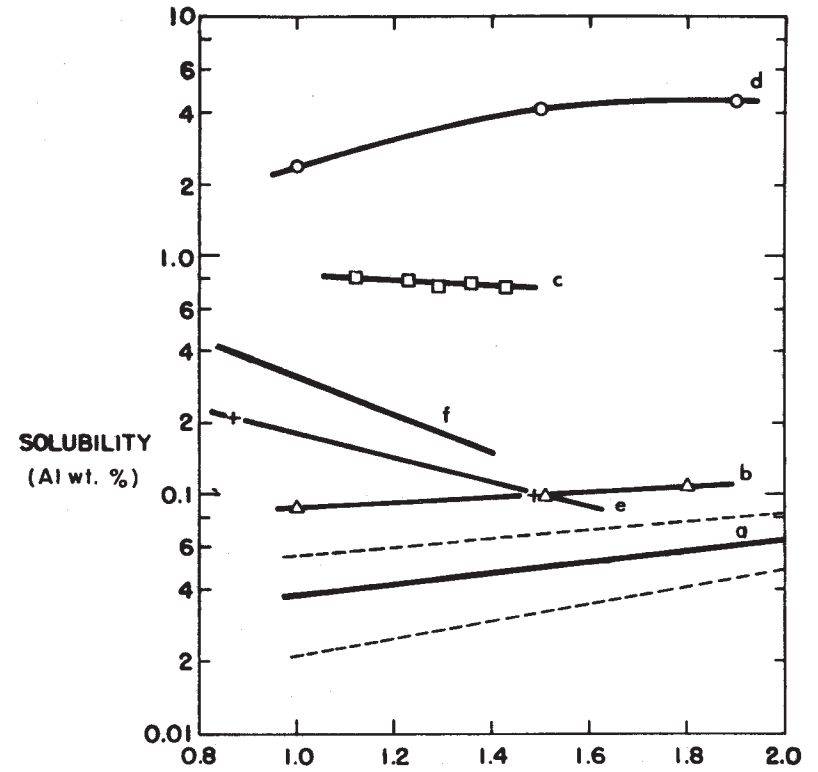


FIGURE 4

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 . |

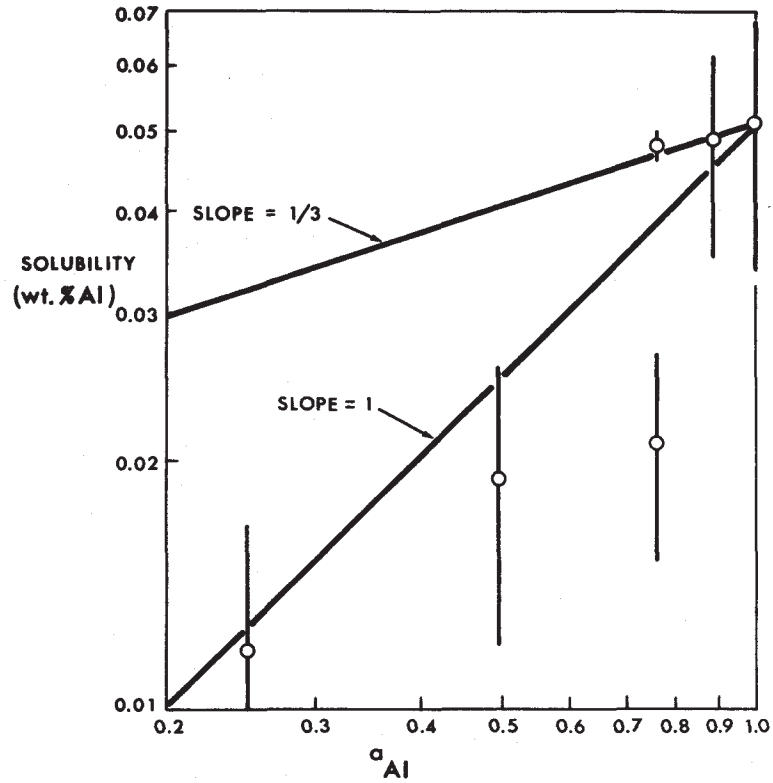


FIGURE 5

Variation of Solubility with activity of Aluminum

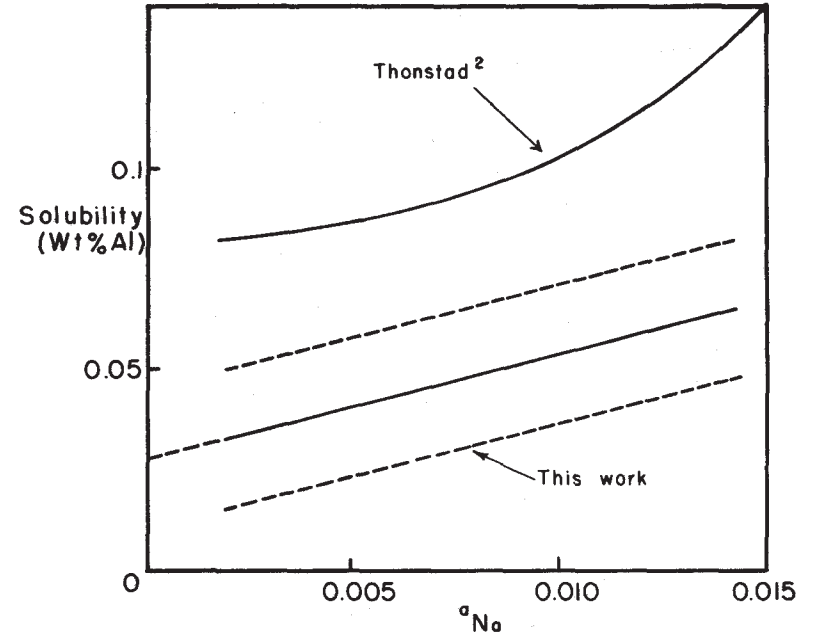


FIGURE 6

Variation of Solubility with Activity of Sodium

REFERENCES

1. W.E. Haupin: *J. Electrochem Soc.*, 1960, vol. 107, pp. 232-236.
2. J. Thonstad: *Canadian J. Chem.*, 1965, vol. 43, pp. 3429-32.
3. J. Gerlach, W. Schmidt, and H. Schmidt: *Erzmetall*, 1967, vol. 20, pp. 111-17.
4. K. Yoshida, T. Ishihara, and G. Yokoi: *Trans. Met. Soc. AIME*, 1968, vol. 242, pp. 233-37.
5. E.W. Dewing: *Trans. Met. Soc. AIME*, 1969, vol. 245, pp. 2181-84.
6. J.D. Edwards, C.S. Taylor, L.A. Cosgrove and A.S. Russell: *J. Electrochem. Soc.*, 1953, vol. 100, pp. 508-12.
7. V.P. Mashovets and V.I. Petrov: *J. Applied Chem.*, (USSR), 1959, vol. 32, pp. 1961-67.
8. K. Matiasovski, M. Malinovsky, and S. Ordzonevski: *J. Electrochem. Soc.*, 1964, vol. 111, pp. 973-76.
9. A.I. Belyaev: *Tsv. Met.* 1957, vol. 30, pp. 70-74.
10. G.A. Abramov: *Trans. Leningrad Ind. Inst. Sect. Met.*, 1939, vol. 1939 (1), pp. 49-59.
11. A.I. Zhurin: *Legkie Metally*, 1937, vol. 6, pp. 27-31.
12. V.P. Mashovets and R.V. Svoboda: *J. Appl. Chem. USSR*, English translation, 1959, vol. 32, pp. 2210-16.
13. T.C. Wilder: *Trans. Met. Soc. AIME*, 1965, Vol. 233, pp. 1202-08.
14. K. Yoshida and E.W. Dewing: In course of publication.
15. R. Battino and H.L. Clever: *Chem. Rev.*, 1966, vol. 66, pp. 395-463.
16. F.D. Richardson and J.C. Billington: *Trans. Inst. Mining and Metallurgy*, 1956, vol. 65, pp. 273-97.