

sodium hydroxide by a current of air at a boiling temperature is a clean-cut method of preparing manganosic oxide.

2. Oxidation at room temperature invariably

leaves in the product an excess of oxygen amounting to a fraction of 1%.

GOAT HILL, LAMBERTVILLE, N. J.

RECEIVED FEBRUARY 14, 1945

[CONTRIBUTION FROM THE CHEMICAL RESEARCH DIVISION, DEPARTMENT OF CHEMICAL ENGINEERING, TENNESSEE VALLEY AUTHORITY, WILSON DAM, ALABAMA]

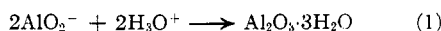
Mechanism of the Precipitation of Alumina from Sodium Aluminate Solutions

BY KELLY L. ELMORE, CHARLES M. MASON AND JOHN D. HATFIELD

In several processes for the production of alumina, alumina trihydrate is precipitated by treating sodium aluminate solution with carbon dioxide. The present paper describes an investigation of the *pH* of sodium aluminate solutions during precipitation of alumina and the determination of the mechanism of precipitation at 60°.

Theory

Alumina in sodium aluminate solutions is believed to occur as NaAlO_2 .¹ The form precipitated from these solutions in the present work was found by X-ray analysis to be gibbsite, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$; this finding is in agreement with the observations of Laubengayer and Weisz.² The precipitation reaction therefore may be postulated as



This reaction is represented by the rate equation

$$-dC_{\text{AlO}_2^-}/dt = k' C_{\text{AlO}_2^-}^2 C_{\text{H}_3\text{O}^+} \quad (2)$$

where $C_{\text{AlO}_2^-}$ represents the concentration of aluminate ion in moles per liter, and t the time in hours. The velocity of the reverse reaction is negligible, since the solubility of gibbsite is small and is practically constant in the *pH* range of this investigation. At constant *pH* equation (2) would reduce to

$$-dC_{\text{AlO}_2^-}/dt = k C_{\text{AlO}_2^-}^2 \quad (3)$$

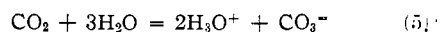
which is the simplest form of the differential equation for a bimolecular reaction. Integration yields

$$1/C_{\text{AlO}_2^-} = kt + \text{const.} \quad (4)$$

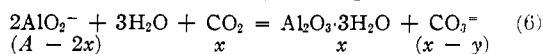
from which it is apparent that a plot of $1/C_{\text{AlO}_2^-}$ versus t at constant *pH* should be a straight line.

The concentration of aluminate ion in moles per liter cannot be calculated exactly from the concentration of alumina found by analysis of the solution, because the analytically determined value represents the sum of the gibbsite, with which the solution may or may not be supersaturated, plus the aluminate ion. It is possible, however, to calculate the change in concentration

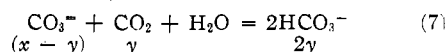
of aluminate ion from the carbon dioxide consumption, because the carbon dioxide added is directly responsible for the conversion of aluminate ion to gibbsite. Let A represent the number of moles per liter of aluminate ion initially present in the solution, x the number of moles per liter of carbon dioxide reacting with the aluminate ion, and y the number of moles per liter of carbon dioxide reacting with the carbonate ion to form bicarbonate ion. If the equation for the formation of carbonic acid



is added to equation (1), the equation



is obtained for the carbon dioxide used to precipitate the alumina. For the carbon dioxide used in converting carbonate to bicarbonate, the equilibrium equation may be written



If the carbon dioxide consumed in converting carbonate to bicarbonate is applied as a correction to the total carbon dioxide consumed, the remainder should represent the amount required for conversion of aluminate ion to gibbsite. The sum, $x + y$, represents the total number of moles per liter of carbon dioxide added to the solution.

For the second ionization of carbonic acid the equations are:



$$K_2 = \frac{(\text{CO}_3^{2-})(\text{H}_3\text{O}^+)}{(\text{HCO}_3^-)(\text{H}_2\text{O})} = \frac{C_{\text{CO}_3^{2-}} f_{\text{CO}_3^{2-}} (\text{H}_3\text{O}^+)}{C_{\text{HCO}_3^-} f_{\text{HCO}_3^-} (\text{H}_2\text{O})} \quad (9)$$

where f is the stoichiometric ionic molar activity coefficient. Substitution of the equalities

$$C_{\text{CO}_3^{2-}} = x - y \quad (10)$$

$$C_{\text{HCO}_3^-} = 2y \quad (11)$$

into equation (9) yields the equation

$$K_2 = \frac{(x - y) f_{\text{CO}_3^{2-}} (\text{H}_3\text{O}^+)}{2y f_{\text{HCO}_3^-} (\text{H}_2\text{O})} \quad (12)$$

By extrapolation of the values of Harned and Scholes³ for lower temperatures, K_2 at 60° was estimated to be 7.35×10^{-11} . Activity coefficients, f , for carbonate and bicarbonate ions were

(3) H. S. Harned and S. R. Scholes, *ibid.*, **63**, 1706-1709 (1941).

(1) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 5, Longmans, Green & Co., London, 1929, p. 285.

(2) A. W. Laubengayer and R. S. Weisz, *THIS JOURNAL*, **65**, 247-249 (1943).

obtained from Walker, Bray and Johnston,⁴ the ionic strengths of the solutions having been calculated to be in the range 0.6 to 0.7. Since the ratio of these ionic activities was employed, small differences in the values selected for the activity coefficients would have little effect on the result. Activity of the water was calculated from Raoult's law. Equation (12) was then rewritten into the form

$$\frac{x}{y} = R = 1 + \frac{14.70 \times 10^{-11}(\text{H}_2\text{O})f_{\text{HCO}_3^-}}{(\text{H}_2\text{O}^+)f_{\text{CO}_3^-}} \quad (13)$$

Calculation of R at various values of pH yields the equation

$$y = x/R \quad (14)$$

which on substitution into the equation

$$C_{\text{CO}_2} = x + y \quad (15)$$

yields

$$x = C_{\text{CO}_2}/(1 + 1/R) \quad (16)$$

where C_{CO_2} is the concentration of carbon dioxide consumed by the reaction in time t , expressed in moles per liter, and x is the extent to which reaction (1) has proceeded.

Experimental

The sodium aluminate solutions used in the investigation were obtained from a pilot plant in which the lime-sinter soda-leach process of alumina extraction⁵ was under study. A typical solution contained 16 g. of Na_2O and 20 g. of Al_2O_3 per liter (mole ratio $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3$, 1.3). The principal impurity was silica, which was present in concentrations of 30 to 180 mg. per liter.

It was first necessary to devise means to measure the pH of alkaline solutions of sodium aluminate in the range 9 to 12.5 in the presence of carbon dioxide and without contamination of the solutions with silica from glass containers. It was then necessary to effect the measurement

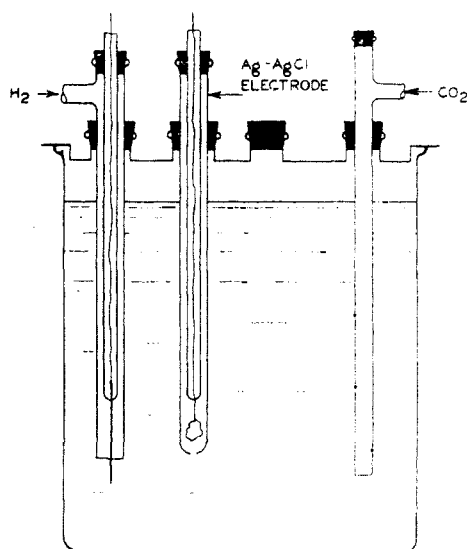


Fig. 1.—Silver cell for pH measurement in alkaline solutions.

(4) A. C. Walker, U. B. Bray and J. Johnston, *THIS JOURNAL*, **49**, 1235-1256 (1927).

(5) R. L. Copson, J. H. Walthall and T. P. Hignett, *Trans. Am. Inst. Mining and Met. Eng.*, **159**, 241-254 (1945).

of the rate of precipitation of the alumina from the solutions by carbon dioxide at constant pH .

In the initial stages of the work, the hydrogen electrode and the National Technical Laboratories No. 1190E glass electrode were found to be well suited for pH measurements in alkaline solutions at 60° . The observation with respect to the 1190E glass electrode was confirmed shortly thereafter in a publication by Kuentzel, Hensley and Bacon.⁶ In sodium aluminate solutions, however, the crust of precipitated alumina soon spoiled the glass electrode, whereas the hydrogen electrodes were easily cleaned and replated for subsequent use. The hydrogen electrodes used were of the Hildebrand⁷ type with a platinized 20-gage platinum wire as the element.

Contrary to the experience of Britton and Welford⁸ and that of Kuentzel, Hensley and Bacon,⁶ the calomel half cell was found to be unsatisfactory at 60° as its potential drifted from day to day. This observation was confirmed by correspondence with the Leeds and Northrup Company.⁹ The literature¹⁰ indicated that the thermal electrolytic type of silver-silver chloride electrode was stable at 60° . This electrode was employed with decinormal potassium chloride to make a reference half cell which was found to be entirely satisfactory since its potential was stable for as long as two weeks.

All pH measurements were made in the apparatus shown in Fig. 1. The apparatus was constructed of fine silver, with exception of the tube that contained the silver-silver chloride electrode. Good electrical insulation was secured by making this tube of glass, the outside surface of which was coated with platinum and heavily silver plated. The cell was maintained at $60 \pm 0.1^\circ$ in a thermostat and was calibrated frequently with standard buffers.⁸ Electrolytic hydrogen, freed of oxygen by passage over hot copper at 450° and humidified by saturators in the thermostat, was supplied to the hydrogen electrode at approximately atmospheric pressure. The observed potentials were corrected to one atmosphere of hydrogen pressure.

The addition of carbon dioxide to sodium aluminate solutions simultaneously lowers the pH and precipitates the alumina as the trihydrate. This process is essentially the titration of sodium aluminate with carbonic acid. During such titrations it was observed that if the flow of carbon dioxide were stopped, precipitation of the alumina continued for some time with an attendant rise in the pH of the solution. This observation indicated that if the carbon dioxide were added at a rate just sufficient to counteract the tendency toward rise in pH , a constant pH could be maintained during the precipitation. This method of control was applied successfully in subsequent studies of the rate of precipitation. Control of the pH was made automatic by attaching the cell (Fig. 1) to a Leeds and Northrup Micromax controller wired to cover the range 0 to 2.5 v. in 10-millivolt steps. The instrument controlled the carbon dioxide supplied to the system through a solenoid valve. The runs could be extended for periods as long as sixteen hours with an over-all variation in pH of ± 0.02 unit as determined by measurements with a Leeds and Northrup type K potentiometer.

Results

All the titration curves obtained in the precipitation of alumina with carbon dioxide, of which Fig. 2 is a typical example, showed a sharp break in pH at the point of incipient turbidity. The average pH at the point of incipient turbidity

(6) L. E. Kuentzel, J. W. Hensley and L. R. Bacon, *Ind. Eng. Chem.*, **35**, 1286-1289 (1943).

(7) J. H. Hildebrand, *THIS JOURNAL*, **35**, 847-871 (1913).

(8) H. T. S. Britton and G. Welford, *J. Chem. Soc.*, 1846-1852 (1937).

(9) Private communication.

(10) W. J. Hamer, *Trans. Electrochem. Soc.*, **72**, 45-70 (1937); H. S. Harned, *THIS JOURNAL*, **51**, 416-427 (1929); H. S. Harned and R. H. Ehlers, *ibid.*, **55**, 2179-2193 (1933); J. K. Taylor and E. R. Smith, *J. Research Natl. Bur. Standards*, **22**, 307-314 (1939).

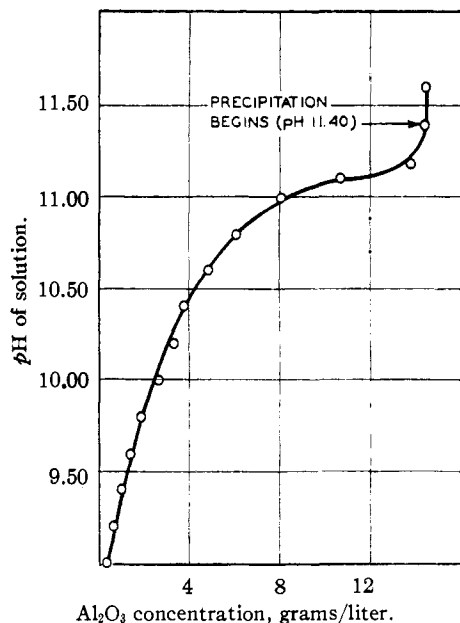


Fig. 2.—Carbon dioxide titration of sodium aluminate solution at 60°.

was found to be linear with the reciprocal of the absolute temperature and to fit the empirical equation $\text{pH} = 2524/T + 3.82$ over the temperature range 30 to 60°.

A typical curve obtained for precipitation at constant pH with automatic control is shown in Fig. 3. Equations (6) and (16) and the initial

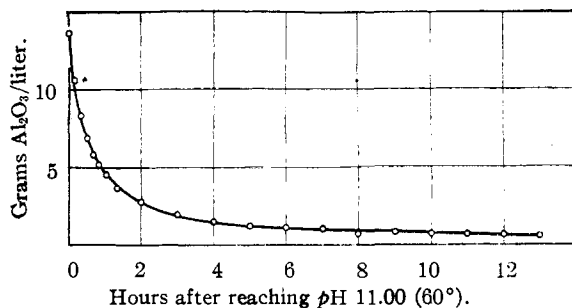


Fig. 3.—Precipitation of $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ from sodium aluminate solution at constant pH with automatic control at 60°.

concentrations of aluminate ion were used to calculate concentrations of aluminate ion in moles per liter. Plots of these calculated concentrations are given for runs at three pH values in Fig. 4. Since preliminary work had shown that the reciprocal of the concentration of aluminate ion, as calculated from total alumina in the solution, was also a straight-line function of time, values so calculated are included as broken lines in Fig. 4 to enable a comparison between the two methods of calculation. The reciprocal of the concentration of alumina, as determined by precipitation as the hydrate and subsequent ignition

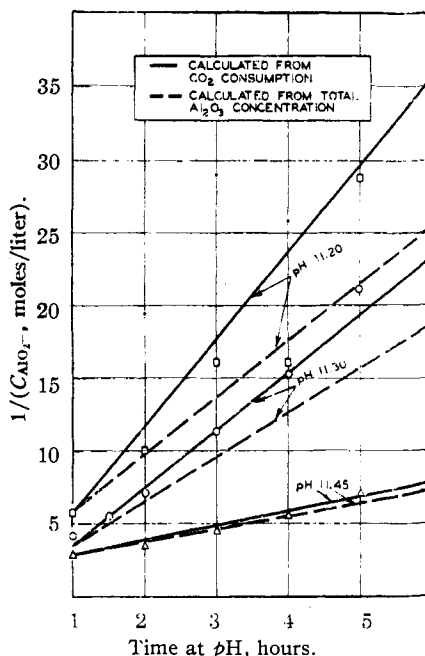


Fig. 4.—Second order rate curves for precipitation of alumina from sodium aluminate solutions at 60°.

to the oxide, is plotted as a function of time in Fig. 5; runs at lower pH values, for which no carbon dioxide analyses were obtained, also are included. It will be noted that the results become more erratic with decrease in pH. Values for the concentration of alumina during the first hour were not reproducible and therefore are omitted from Figs. 4 and 5.

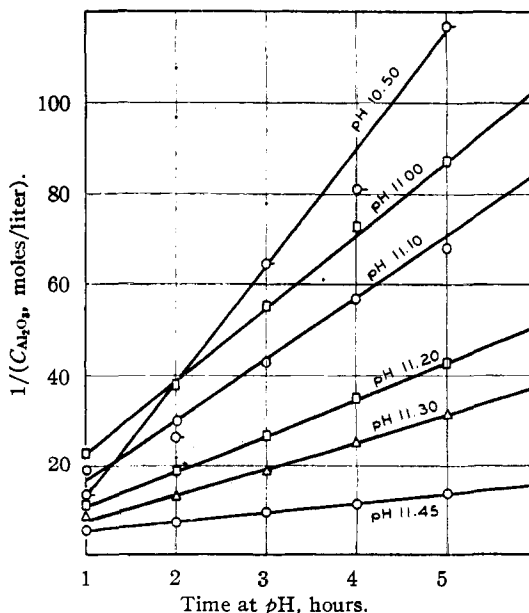


Fig. 5.—Reciprocal of total alumina content of sodium aluminate solutions as a function of time and pH at 60°.

The straight-line relationships shown in Figs. 4 and 5 are taken as ample evidence that the reaction proposed in equation (1) represents the precipitation reaction at 60°.

Table I shows, for three runs, the differences between the concentrations of aluminate ion as calculated from the carbon dioxide absorbed and from the analysis of the solutions for total alu-

TABLE I
DIFFERENCES BETWEEN CONCENTRATIONS OF ALUMINATE ION AS CALCULATED FROM TOTAL ALUMINA AND FROM CARBON DIOXIDE ABSORBED

Time, hr.	Excess of AlO_2^- as calculated from total Al_2O_3 concentration over that calculated from CO_2 absorption, moles/liter		
	pH 11.20	pH 11.30	pH 11.45
1	0.006	0.007	0.002
2	.008	.013	.008
3	.013	.022	.007
4013	...
5	.012	.017	.005
6	.015	.010	.004
7012	...
8012	...
Av.	.011	.013	.005

mina. The differences suggest, as a rough approximation, that the solubility of gibbsite is about 5×10^{-3} mole per liter in sodium aluminate solutions of pH 11.20 to 11.45 and ionic strength 0.6 to 0.7.

Acknowledgment.—The investigation was made at the suggestion of R. L. Copson, Chief of Chemical Research and Engineering. Gray Lucas and E. R. Rushton assisted in the experimental work.

Summary

1. A method was developed for measurement of the pH of alkaline solutions containing carbon dioxide without their contamination by silica.
2. The equation $2\text{AlO}_2^- + 2\text{H}_3\text{O}^+ \rightarrow \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ was found to represent the mechanism of the precipitation of alumina from sodium aluminate solutions by carbon dioxide at 60°.
3. The solubility of gibbsite in sodium aluminate solutions of ionic strength 0.6 to 0.7 and pH 11.20 to 11.45 was estimated to be about 5×10^{-3} mole per liter.

WILSON DAM, ALABAMA

RECEIVED MARCH 9, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

Studies in Stereochemistry. VII. The Effect of F-Strain on the Relative Base Strengths of Ammonia and the Ethylamines

BY HERBERT C. BROWN

In previous papers of this series, the need of considering both polar and steric factors in theorizing has been pointed out. For example, if only the polar effect of the methyl group (+I) is considered, it would be predicted that the strength of ammonia and the methylamines as bases should increase regularly with the number of methyl groups. However, this order, $\text{NH}_3 < \text{CH}_3\text{NH}_2 < (\text{CH}_3)_2\text{NH} < (\text{CH}_3)_3\text{N}$ (Fig. 1, curve A), is not observed. Instead, operation of the steric factor causes B-strain,¹ which slightly reduces the strength of dimethylamine and markedly reduces that of trimethylamine. As a consequence, the order of base strength observed with the aid of acids with relatively low F-strain factors, such as hydrogen chloride and trimethylboron, is $\text{NH}_3 < (\text{CH}_3)_3\text{N} < \text{CH}_3\text{NH}_2 < (\text{CH}_3)_2\text{NH}$ (Fig. 1, curve B). Reference acids with higher F-strain factors should cause the observed order to change successively to C, D, E, and, finally, to F (Fig. 1). Actually, the order $(\text{CH}_3)_3\text{N} < (\text{CH}_3)_2\text{NH} < \text{NH}_3 < \text{CH}_3\text{NH}_2$ (curve E) is obtained with the highly hindered reference acid, tri-*t*-butylboron.²

It should be possible to obtain order F, a decrease in base strength with increasing number of

alkyl groups, by slightly increasing the F-strain between the amines and the reference acid. This increase might be accomplished in either of two ways: (1) use of more highly hindered reference acids than tri-*t*-butylboron, or (2) use of larger, bulkier alkyl groups than methyl on the amines.

The first alternative is now being studied at this University; the second forms the subject of the present paper. In it are described the results of an investigation of the relative strengths of ammonia and the ethylamines with three reference acids: hydrogen chloride, trimethylboron, and tri-*t*-butylboron.

Experimental

The preparation and purification of trimethylboron and tri-*t*-butylboron and the experimental techniques are described in previous publications in this series.³

The amines used were Eastman Kodak Company products which had been distilled over sodium and fractionated through a 15-plate column before use.

The comparisons of the relative strengths of the amines with a given reference acid were carried out by the competition method.^{3b} In the case of trimethylboron and tri-*t*-butylboron the results thus obtained were checked by comparisons of the saturation pressure of the individual addition compounds which these acids form with the amines. (There is now considerable evidence to support

(1) Brown, Bartholomew and Taylor, *THIS JOURNAL*, **66**, 435 (1944).

(2) Brown, *ibid.*, **67**, 378 (1945).

(3) See particularly (a) Brown, Taylor and Gerstein, *ibid.*, **66**, 431 (1944), and (b) Brown, *ibid.*, **67**, 374 (1945).