

## EQUILIBRIUM COMPOSITION OF SODIUM ALUMINATE LIQUORS

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An equation has been developed that correlates the equilibrium solubility of gibbsite ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) in both Bayer and pure sodium aluminate liquors. It can be used to predict equilibrium liquor composition as a function of temperature, caustic content, and liquor impurity concentrations. The correlation is based on the theory of uni-univalent ion populations in caustic liquors proposed by Dewey. The correlation also yields identical values for  $\Delta H^\circ_f$  and  $\Delta G^\circ_f$  of the  $\text{AlO}_2^-$  ion to those determined by Hemingway, Robie, and Kittrick, and provides new estimates for the standard entropy and heat capacity of the  $\text{AlO}_2^-$  ion.

Introduction

Knowledge of equilibrium alumina solubility in Bayer plant caustic aluminate liquors is necessary for the development of certain kinetic alumina precipitation models (1). Laboratory experimental data have previously been used to derive equations that allowed predictions of equilibrium solubility of alumina trihydrate (gibbsite) as functions of liquor caustic concentration and temperature for individual liquors from different sources. Because the relative amounts and types of impurities present in these liquors are different, the equilibrium expressions are found to be unique for each liquor. Furthermore, these equilibrium expressions have to be updated periodically as plant liquor compositions change over a period of time, requiring on-going experimental data acquisition and reduction.

A general method of accurately calculating equilibrium liquor compositions as functions of total liquor composition and temperature was desired in order to eliminate the need for individual liquor characterization tests and to simplify modelling efforts. This paper presents one successful approach based on correlations of sodium hydroxide-sodium aluminate-gibbsite equilibrium solubility constants, and on the theory of uni-univalent ion populations in caustic liquors proposed by Dewey (2).

The correlation covers equilibrium solubility data of Russell, et al (3) in pure liquors and in-house experimental data on both Bayer and pure liquors. The correlation yields identical values of  $\Delta H^\circ_f$  and  $\Delta G^\circ_f$  for the  $\text{AlO}_2^-$  ion to those reported by Hemingway et al (4) and new estimates are provided for the standard entropy ( $S^\circ$ ) and heat capacity ( $C_p^\circ$ ) of the  $\text{AlO}_2^-$  ion at 298.15K.

The predicted equilibrium constant from the correlation, along with starting liquor analyses can be used to calculate equilibrium liquor compositions after gibbsite precipitation or dissolution for both Bayer and pure sodium aluminate liquors and the alumina-to-caustic ratio (A/C) is determined within about  $\pm 0.01$ . The results appear to be quite good when evaluated against available equilibrium data in the range of 40-120°C.

Correlation Equation and Definition of Equilibrium Constants for Bayer Liquors

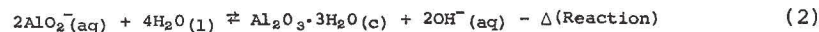
Below is the equation which gives sodium aluminate equilibrium constants for both synthetic and plant liquors:

$$-R \ln K_{eq} = \frac{-64,149}{T} + 69.92 \left[ \frac{(T-298.15)}{T} - \ln T/298.15 \right] + 166.465(1+.005360M) \quad (1)$$

Where:  $K_{eq}$  = liquor equilibrium constant  
 $R$  = universal gas constant (8.31051 J/mol-K)  
 $T$  = absolute temperature K = °C+273.15  
 $M$  = total liquor molality at equilibrium (gm mols/kg H<sub>2</sub>O)

Figure 1 shows the agreement over a range of molalities and temperatures of observed equilibrium constants 'vs' those predicted by the correlation for both pure and Bayer liquors from different sources. The large dots connected by thin lines represent the data of Russell, et al for pure sodium aluminate solutions while the other points represent various in-house data for both pure and Bayer liquors.

As is widely known, the equilibrium alumina-to-caustic ratio (A/C) is directly proportional not only to temperature but to caustic and impurity levels in the liquor. It is expected, therefore, that the equilibrium A/C should be defined by an appropriate function of temperature and of either total ionic strength or molality. Dewey has found that the boiling point rise of Bayer liquors is equal to the boiling point rise of pure sodium hydroxide solutions of equal molality at the same temperature when Bayer liquors are defined as mixtures of monovalent ions (e.g. - OH<sup>-</sup>, Cl<sup>-</sup>, NaCO<sub>3</sub>, NaSO<sub>4</sub>). This shows that the total ionic strength of these liquors is equal to the molality, hence we use molality. The existence of the AlO<sub>2</sub><sup>-</sup> ion rather than the Al(OH)<sub>4</sub><sup>-</sup> ion in plant liquors under boiling conditions is also supported by the available boiling point rise data (2). Since that definition of Bayer liquor molality is so successful for prediction of Bayer liquor boiling points and vapor pressures, the same conventions were used for the definition of liquor equilibrium constants for this work. The balanced equation for gibbsite precipitation may be written as:



The corresponding equilibrium solubility constant is expressed as:

$$K_{eq} = \frac{[OH^-]^2}{[AlO_2^-]^2 [H_2O]^4} \quad (3)$$

In very dilute solutions concentrations usually are expressed in moles per liter or other convenient units but in concentrated solutions concentrations should be expressed in terms of component activities. In this case the activity of water in Bayer liquors can be calculated as a function of total liquor molality and temperature by the relationship for boiling point rise of Bayer liquors given by Dewey (2).

However, the activities of OH<sup>-</sup> and AlO<sub>2</sub><sup>-</sup> in solution are unknown and are thus replaced by their respective mole fractions or molalities in the equilibrium expression on the assumption that the ratio of the concentrations is an

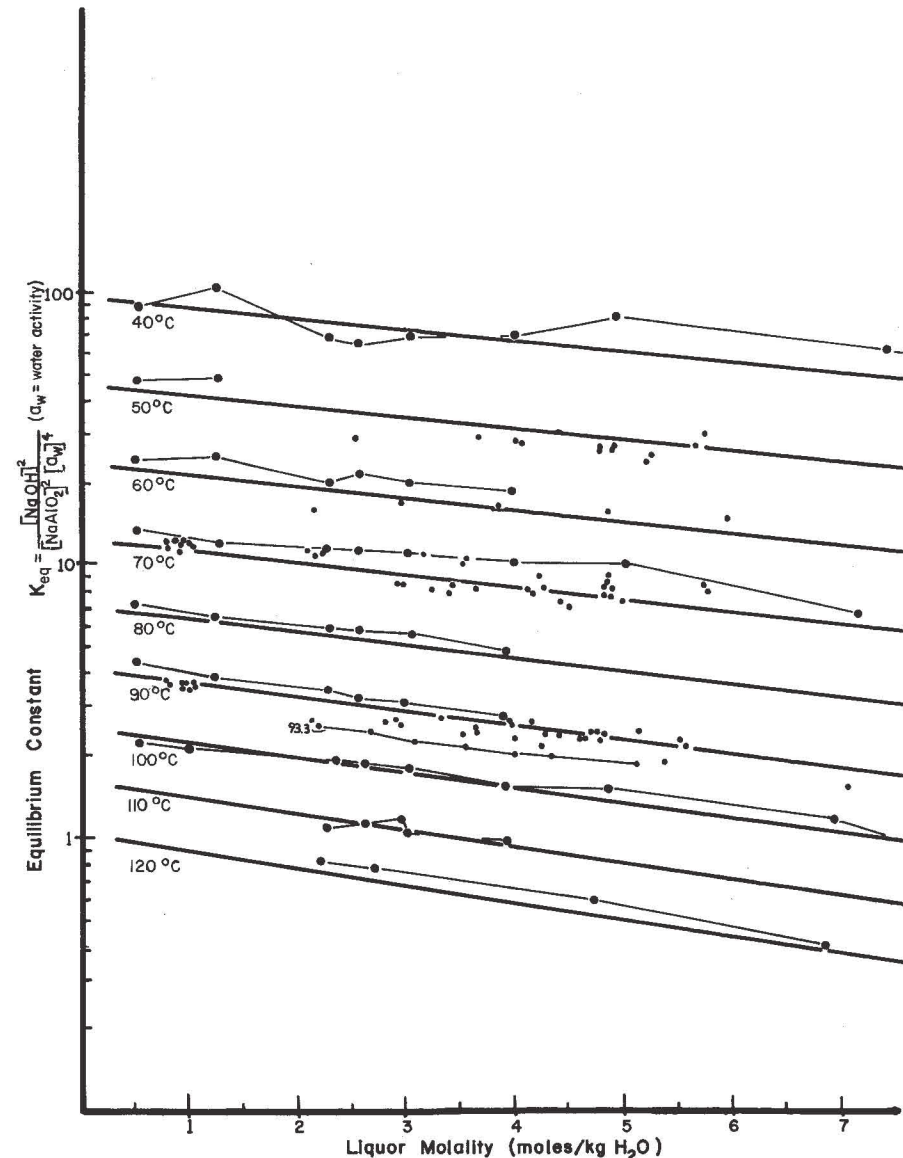


Figure 1  
Sodium Aluminate Liquor Equilibrium Solubility

approximation of the ratio of the activities. The validity of this assumption is supported by the fact that the kinetics of crystallization of gibbsite can be accounted for satisfactorily by using concentrations rather than activities (1)(5)(6).

Liquor equilibrium constants calculated in this manner were then correlated by multiple linear regression techniques to obtain Eq. 1.

Table I shows examples of calculating by iteration liquor equilibrium compositions from starting liquor analyses using the predicted equilibrium constants. Liquor compositions are reported as the conventional C, S, and A values (C and S as g equivalent Na<sub>2</sub>CO<sub>3</sub>/kg liquor; A as g Al<sub>2</sub>O<sub>3</sub>/kg liquor). Liquors #1-#4 are starting liquors for equilibrium tests selected from among 42 in-house equilibrium tests run as described later. Liquors #1 and #2 are roughly equivalent except for impurity levels. Liquor #4 is a dilution of liquor #3.

Calculation of Equilibrium Composition

Calculation of equilibrium liquor composition from starting liquor analyses and predicted equilibrium constants is an iterative process which can be accomplished practically only by computer. The process basically consists of adjusting the amount of alumina trihydrate precipitated from the starting liquor until the liquor equilibrium constants as calculated by Eqs. 1 and 3 become equal.

First the starting liquor molality is calculated from the chemical assay by the methods presented by Dewey (2), p. 10. Equilibrium constants are then calculated at the temperature of interest by Eq. 1 as a function of molality and temperature and Eq. 3 from the chemical assays. Depending on the relative values of the two constants, a prescribed amount of alumina trihydrate will then either be added to or subtracted from the starting liquor and the liquor compositions and equilibrium constants recalculated and recompared. This process is repeated until the constants calculated by Eqs. 1 and 3 are equal.

For optimum numerical accuracy, both liquor composition and molality should be recalculated at each step since as alumina trihydrate precipitates, liquor molality increases.

Extension of the Model to Other Conditions

The data covered by the correlation cover the following ranges:

Temperature	40°-120°C
Molality	0.5-9.6
Free Soda 'C' (gpk)	26.-334.
C/S	0.34-1.0
A/C	0.094-0.710

**Table I. Equilibrium Liquor Composition  
Comparison of Calculated 'vs' Observed Equilibria**

Liquor	Temp. (°C)	g/kg Soln.		A	A/C	Molality* (impurities)	Molality Total
		C	S				
<u># 1 Synthetic</u>	-	167.8	234.9	33.7	.201	0	4.884
<u>Equilibrium Liquor</u>							
Calculated	50	167.3	234.1	35.7	.214	0	4.875
Observed	50	163.4	232.2	35.4	.217	0	4.797
Calculated	90	157.0	219.8	73.5	.468	0	4.693
Observed	90	158.0	221.9	74.0	.468	0	4.747
<u># 2 from 143 °C</u>	-	162.9	227.9	32.8	.201	0.349	5.050
<u>Digestion</u>							
<u>Equilibrium Liquor</u>							
Calculated	50	162.2	226.9	35.4	.218	0.350	5.038
Observed	50	157.1	223.2	34.4	.219	0.339	4.902
Calculated	90	152.5	213.3	72.3	.474	0.333	4.852
Observed	90	151.1	212.2	71.5	.473	0.329	4.809
<u># 3 from 240 °C</u>	-	189.7	217.5	35.1	.185	1.039	5.845
<u>Digestion</u>							
<u>Equilibrium Liquor</u>							
Calculated	50	186.5	213.9	45.4	.244	1.025	5.785
Observed	50	184.0	213.6	42.3	.230	1.018	5.731
Calculated	90	173.7	199.2	87.0	.501	0.969	5.534
Observed	90	171.9	200.0	86.2	.501	0.974	5.530
<u># 4 Dilution of Liquor # 3</u>	-	43.0	49.3	7.9	.184	0.145	1.058
<u>Equilibrium Liquor</u>							
Calculated	90	42.5	48.8	14.8	.348	0.144	1.052
Observed	90	41.6	49.5	14.4	.346	0.146	1.053

(\*includes all impurities except Na<sub>2</sub>CO<sub>3</sub>)

Extension of this model outside of the stated temperature range is discouraged, especially at temperatures over 120°C (e.g. digestion conditions). At higher temperatures the increasing rate of conversion of gibbsite to alumina monohydrate (boehmite) provides an unknown mixture containing gibbsite, boehmite, and possibly intermediate transition forms, thus rendering equilibrium expressions for gibbsite alone useless.

#### Experimental Procedure for Developing Equilibrium Data

The correlation includes 146 data points obtained from three sources.

There are 48 cases taken from previously run equilibrium tests from various in-house experimenters where "super-saturated" liquors were contacted with alumina trihydrate at high seed charges and tumbled in polypropylene bottles end-over-end for times ranging from 24 hours for the 90°C tests to 96 hours for the 50° and 70°C tests. The liquors and seeds were obtained from several different commercial Bayer plants.

Also included are data from 42 tests run in pairs in order to approach equilibrium both by precipitation and by dissolution of alumina trihydrate. The starting liquor A/C's were adjusted by synthetic liquor addition to about 0.20 (below saturation) and then samples were split into two fractions, each seeded with identical alumina trihydrate charges. One fraction was then heated (100-110°C) overnight to dissolve a portion of the seed and raise the A/C to supersaturate the solution at the temperature of interest. Both samples were then tumbled at temperature for times ranging from 168 hours (7 days) for the 70° and 90°C tests to 240 hours (10 days) for the 50°C tests. As expected, the two samples were found to be virtually identical in composition after the prescribed interval.

The remaining 56 data cases are those of Russell, et al (3).

#### Thermodynamic Considerations

The gibbsite equilibrium solubility constant  $K_{eq}$  is defined by Eq. 3 wherein the activity ratio ( $OH^-/AlO_2^-$ ) has been replaced by the ratio of the respective molalities or mol fractions of  $OH^-$  and  $AlO_2^-$ . The activity of  $H_2O$  has been assumed to be equal to the ratio of the solution pressure to the vapor pressure of pure water at the solution temperature. The solution pressure was calculated with the aid of the boiling point elevation relation previously presented by Dewey. The aluminate ion ( $AlO_2^-$ ) rather than the tetrahydroxy ion ( $Al(OH)_4^-$ ) is chosen as the species existing in the concentrated solutions. This choice is not in agreement with the conclusions of Moolenaar et al (10) from infra-red and Raman spectra studies but was found by Dewey to be necessary to obtain a 1:1 correspondence at equal molalities between the activity of

water in NaOH solutions and in both pure and impure sodium aluminate solutions. The results obtained will be shown to agree well with the results of others.

The equilibrium constant  $K_{eq}$  is related to thermodynamic properties by the relations:

$$-RT \ln K_{eq} = \Delta G(R) = \Delta H(R) - T\Delta S(R) \quad (4)$$

and to  $\Delta C_p(R)$  through the relations

$$\Delta H(R, T) = \Delta H(R, 298) + \int_{298}^T \Delta C_p(R) dT \quad (5)$$

$$\Delta S(R, T) = \Delta S(R, 298) + \int_{298}^T \Delta C_p(R)/T dT \quad (6)$$

Nearly all the thermodynamic values required to solve for  $\Delta G^\circ(R)$  at standard conditions (298.15K, M=0) are available in the literature, from determinations which did not depend on the data sets used in the present study. Selected values are tabulated in Table II, along with the  $\Delta$ (Reaction) values for the precipitation of gibbsite (Eq. 2).

A regression analysis over the values of  $-R \ln K_{eq}$ , using the form of Eq. 1 with no preset coefficients, gave a value of  $\Delta H^\circ(R)$  of  $-63408 \pm 2400$  J/mol. This value differs from the literature value of Table II by less than the probable error of either value, but the coefficient of the heat capacity term (second variable term) did not differ statistically from zero. Subsequent regressions of the data were made with preset values of  $\Delta H^\circ(R)$  to avoid statistical confounding of  $\Delta H^\circ(R)$  and  $\Delta C_p(R)$ .

Derived data from regressions with  $\Delta H^\circ(R) = -64149$  J/mol and three different assumed forms for  $\Delta C_p$  are listed in Table III. The three regressions fit the data equally well, both statistically and by graphical comparison as in Figure 1. The simplest form,  $\Delta C_p(R) = \text{constant}$ , is shown on Figure 1 and used in equilibrium calculations.

For thermodynamic analysis, however, the presence of a term involving molality in the entropy portion of  $\Delta G(R)$  suggests that a molality term also should be present in the heat capacity term. It can be seen in Table II that results for the two heat capacity forms comprising molality are identical, except for the coefficients of the different molality terms. Thus it appears unlikely that a particular form for  $\Delta C_p(R)$  can be determined by regression analysis of the data used for this report.

Table IV presents the results of a series of regressions over a range of values of  $\Delta H^\circ(R)$ , using  $\Delta C_p(R) = a + bM/T$ . Coefficients of the two terms involving molality are relatively constant. However, coefficients of the other terms (estimate of values at infinite dilution) vary substantially and

Table III. Regression-Derived Thermodynamic Values at 298.15K for  $\Delta H^\circ(R) = -64149$  and Three Assumed Forms of  $\Delta C_p(R)$

Form - $\Delta C_p(R) =$	a	a+bM	a+bM/T
$\Delta H^\circ(R)$	-64149	-64149	-64149
$\Delta S(R)$	-166.5-0.89M	-167.1-0.723M	-167.1-0.718M
$\Delta C_p(R)$	69.92	120.24-13.6M	120.71-4474M/T
$\Delta G^\circ(R)$ (298.15, M=0)	-14507	-14328	-14328
$\Delta S^\circ(R)$ (298.15, M=0)	-166.5	-167.1	-167.1

Table IV. Effect of Varying  $\Delta H^\circ(R)$  on Thermodynamic Properties at 298.15K

$\Delta H^\circ(R)$ J/mol	$\Delta G^\circ(R)$ J/mol	$\Delta S(R) = \Delta S^\circ + CM$		$\Delta C_p(R) = a+b M/T$	
		$\Delta S^\circ$ J/K-mol	C	a J/K-mol	b
-64149	-14328	-167.1	-.718	120.7	-4474.
-64567	-14363	-168.4	-.720	128.7	-4452.
-64986	-14389	-169.7	-.722	136.6	-4429.
-65317	-14415	-170.7	-.725	142.6	-4393.
-65404	-14421	-171.0	-.725	144.2	-4389.
-65823	-14452	-172.3	-.728	152.1	-4364.
-66241	-14484	-173.6	-.731	159.8	-4326.
Std. Error	±300.	±1.	±0.09	±23.	±1800.

Table II. Literature Values of Thermodynamic Properties at Standard Conditions (298, 25K, M=O)

	$\Delta H^\circ_f$ J/mol	Ref.	$\Delta G^\circ_f$ J/mol	Ref.	$S^\circ$ J/K-mol	Ref.	$\Delta S^\circ_f^*$ J/K-mol	$C_p$ J/K-mol	Ref.
$Al_2O_3 \cdot 3H_2O$ (Gibbsite)	-2,586,260 ±2,380	(4)	-2,309,780 ±2,400	(4)	136.88 ±0.28	(8)	-926.58	183.40	(8)
$Al_2O_3 \cdot H_2O$ (Boehmite)	-1,986,200 ±4,400	(7)	-1,836,800 ±4,100	(7)	96.86	(9)	-498.423	131.25	(9)
$H_2O(l)$	-285,830	(9)	-237,178	(9)	69.915	(9)	-163,174	75.291	(9)
$OH^-(aq)$	-229,995	(9)	-157,293	(9)	-10.75	(9)	-243.84	-148.53	(9)
$AlO_2^-(aq)$	-918,806	(9)	-830,900 ±2,100	(7)	-21.	(9)	-294.57	-	-
$\Delta(R)$	-65,317	-	-13,583	-	-122.45	-	-172.42	-	-

(\*calculated by authors from  $S^\circ$  for the compounds and from  $\Delta G^\circ_f = \Delta H^\circ_f - T\Delta S^\circ_f$  for the ions.)

uniformly as  $\Delta H^\circ(R)$  is varied. Thus the values at standard conditions that can be assigned to  $\Delta S^\circ(R)$  and  $\Delta C_p(R)$  from the present work depend uniquely on the selected value of  $\Delta H^\circ(R)$  and it follows that the accuracy of the values also depends on the accuracy of the selected  $\Delta H^\circ(R)$ .

The best available independent value of  $\Delta H^\circ(R)$  from Table II (-65317 J/mol hydrate precipitated) yields the values

$$\begin{aligned} \Delta G^\circ(R) &= -14415 \\ \Delta S^\circ(R) (298.15) &= -170.7 - 0.725M \\ \Delta C_p(R) &= 142.6 - 4393M/T \end{aligned}$$

Using these values and the other data in Table II to recalculate the properties of the  $AlO_2^-(aq)$  ion yields, at 298.15K and  $M=0$ ,

Calculated	Literature (Table II)
$\Delta H^\circ_f = -918,806$ J/mol (accepted)	-918,806
$\Delta G^\circ_f = -830,622$ J/mol	-830,900
$\Delta S^\circ_f = -295.4$ J/K-mol	-294.57
$C^\circ_p = -278.7$ J/K-mol	_____
$S^\circ = +3.21$ J/K-mol	-21

Thus values for  $\Delta H^\circ_f$  and  $\Delta G^\circ_f$  from the present work are entirely consistent with the literature values from independent studies. Therefore it is believed that the estimates of  $C^\circ_p$  and  $S^\circ$  for the aluminate ion are credible, since at  $M=0$  the assumed relation,  $a(OH^-)/a(AlO_2^-) = M(OH^-)/M(AlO_2^-)$  is true and introduces no error. This may not be true for  $M>0$ .

### Boehmite Solubility Relation

Equation (2) may be rearranged to give:

$$2(AlO_2^- - OH^-)_{(aq)} = Al_2O_3 \cdot 3H_2O_{(c)} - 4H_2O_{(l)} - \Delta(R) \quad (7)$$

and solved for values of  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta C^\circ_p$  of the bracketed term using appropriate values from Tables II and IV ( $\Delta C_p(T)$  also may be obtained by using heat capacity-temperature relations for gibbsite and water). The bracketed term may then be substituted into a similar relation for boehmite to obtain  $\Delta(R)$  for boehmite from which the equilibrium solubility constant relation can be obtained. Assuming  $\Delta C_p(R)$  equals a constant and using the data for  $\Delta H^\circ_f$ ,  $\Delta S^\circ_f$ , and  $C^\circ_p$  for gibbsite, boehmite, and  $H_2O$  from Table II and  $\Delta(R)$  from Table III, the equilibrium constant for boehmite is:

$$-R \ln K_{eq}(\text{Boehmite}) = \frac{-35752}{T} + 168.1 \left[ \frac{T-298.15}{T} - \ln T/298.15 \right] + 66.647 + 0.891 M \quad (8)$$

This equation yields larger values of  $K_{eq}$  than obtained by Russell et al (3), i.e., a lower solubility of boehmite. The difference may be due to structural differences between the boehmite precipitates of Russell et al and those used for developing the thermodynamic data. Hemingway, Robie, and Kittrick (7) have criticized the  $S^\circ$  and  $C_p$  data on the basis that the boehmite used had a Bayerite x-ray spectrum. It is also known that boehmites produced by hydrolysis of gibbsite have variable amounts of interstitial water which might affect the thermodynamic properties. More work is needed on boehmite.

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