

THE HEAT OF DISSOLUTION OF GIBBSITE AT BAYER DIGESTION TEMPERATURES

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The heat of reaction of gibbsite in caustic solution has been reported by various sources; the average value being 140 kcal/kg Al_2O_3 . Although this value has been determined from solubility or calorimetric data at normal Bayer precipitation temperatures, it has been widely used in Bayer process mass and energy calculations at digestion temperatures. However, using correlations for gibbsite and Bayer liquor heat capacity, and National Bureau of Standards heats of formation data, the heat of dissolution of gibbsite at Bayer digestion temperatures (145°C) has been calculated at 200 kcal/kg Al_2O_3 . This paper describes the theoretical thermodynamic treatment and the experimental verification (by calorimetry) of this higher value.

Introduction

In normal Bayer process digestion, gibbsite in bauxite dissolves in caustic liquor to yield an alumina-rich solution. This process is endothermic. The energy required to dissolve gibbsite is a significant part of the total energy used in digestion. Any mass and energy balance calculation attempting to accurately predict digestion steam consumption requires some value or correlation for the heat of dissolution of gibbsite.

A review of available literature shows a wide range of values of heat of dissolution/crystallization of gibbsite. Several reported values are found in Table I. Of the sources listed, all but one obtained their value from equilibrium solubility measurement. An equilibrium constant, K , was determined from solubility data and was related to heat of dissolution, ΔH_D , by the relation:

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta H_D}{RT^2} \quad (1)$$

where T is temperature and R is the universal gas constant. In most cases, ΔH_D was determined from solubility data taken at Bayer process precipitation conditions (40–80°C), only Russell (6) used solubility data above 100°C. Calvet's (9) value was determined calorimetrically at 35.5°C.

The average of the Table I values is 140 kcal/kg Al_2O_3 . This average value (or one close to it) has been widely used in Bayer process mass and energy calculations. It has been used in both digestion and precipitation calculations, even though it is based on data taken at precipitation conditions only.

Because of the lack of data for gibbsite heat of dissolution at digestion temperature (130–150°C), a method was sought to determine that value from available thermodynamic data. Using available correlations for Bayer liquor and gibbsite heat capacity and National Bureau of Standards heat of formation data, a significantly higher than expected heat of dissolution value was determined at 145°C. This higher value was verified experimentally (again at 145°C) through use of the SETARAM C-80 heat flux calorimeter.

TABLE I

REPORTED HEATS OF DISSOLUTION OF GIBBSITE

Russell (6)	144.0 kcal/kg Al_2O_3
Adamson (7)	170.0
Bagaev (8)	137.0
Calvet (9)	109.8
Tomonari (10)	135.3
Kuznetsov (11)	137.2

CALCULATION OF ΔH_D

Figure 1 shows diagrammatically how the heat of dissolution of gibbsite can be calculated. If low ratio spent liquor and gibbsite are present at temperature T, the amount of heat required to dissolve the gibbsite and form a high ratio liquor is ΔH_D . ΔH_D is the heat of dissolution of gibbsite at temperature T.

Because the energy required to form green liquor from spent liquor and hydrate is independent of the path chosen, the calculation of ΔH_D can be broken down into four steps:

1. Calculate the amount of heat required to take the reactants (spent liquor and gibbsite) from temperature T to a base temperature T_0 . If this is defined as ΔH_1 , it can be determined from:

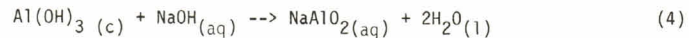
$$\Delta H_1 = M_{SL} \int_T^{T_0} C_{PL} dT + M_G \int_T^{T_0} C_{PG} dT \quad (2)$$

where M_{SL} and M_G are mass of spent liquor and gibbsite, respectively and C_{PL} and C_{PG} are equations for liquor and gibbsite heat capacity.

2. Calculate the amount of heat to take reactants at T_0 , to products at T_0 . Defining this as ΔH_2 and T_0 as 25°C, ΔH_2 can then be determined from standard heats of formation (ΔH_{fi})

$$\Delta H_2 = \sum \Delta H_f \text{ products} - \sum \Delta H_f \text{ reactants} \quad (3)$$

Consider the reaction



then:

$$\Delta H_2 = \Delta H_f(NaAlO_2) + 2\Delta H_f(H_2O) - \Delta H_f(NaOH) - \Delta H_f(Al(OH)_3) \quad (5)$$

3. Calculate the amount of heat required to take the product (green liquor) from T_0 to T. Defining this as ΔH_3 , then:

$$\Delta H_3 = (M_{SL} + M_G) \int_{T_0}^T C_{PL} dT \quad (6)$$

4. Calculate the desired ΔH_D by adding the previous terms.

$$\Delta H_D = \Delta H_1 + \Delta H_2 + \Delta H_3 \quad (7)$$

Table II gives equations for C_{PL} and C_{PG} , and Table III gives values of ΔH_f used to determine ΔH_D .

FIGURE 1. HEAT OF DISSOLUTION CALCULATION DIAGRAM

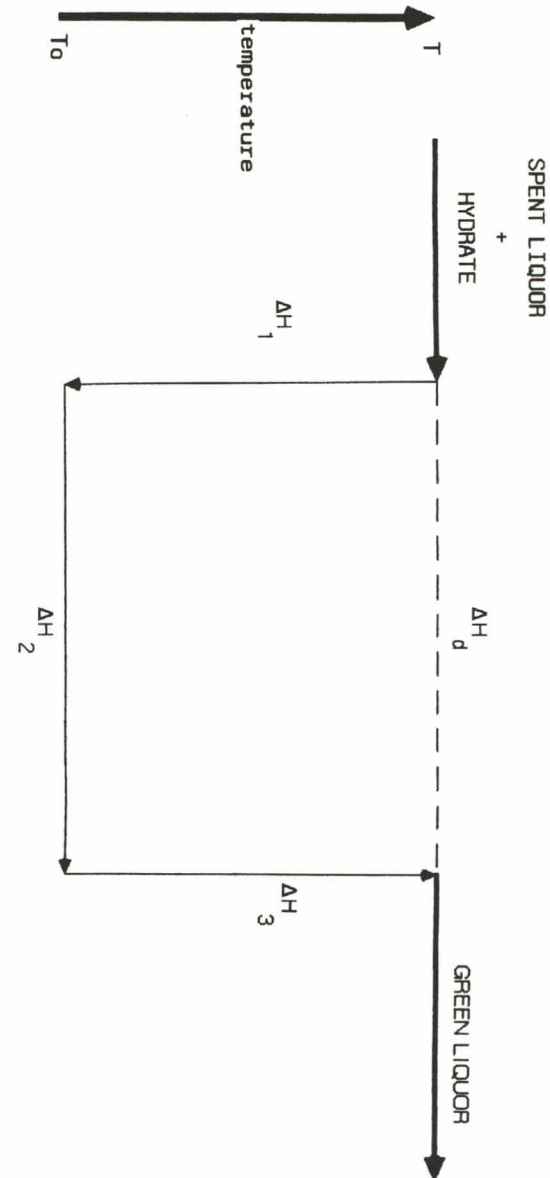


TABLE II

HEAT CAPACITY EQUATION FOR BAYER LIQUOR AND GIBBSITE

$$C_{pL} = .99639 - 3.90998 \times 10^{-4} (TC) - 5.3832 \times 10^{-4} (Al_2O_3) + 2.46493 \times 10^{-7} (TC^2) + 5.7186 \times 10^{-7} (TC) (Al_2O_3) - 1.86581 \times 10^{-7} (Al_2O_3) (T) - 1.07766 \times 10^{-7} (TC) (T) - 1.51278 \times 10^{-4} (T) + 2.1464 \times 10^{-6} (T^2)$$

where C_{pL} is the heat capacity of Bayer liquor (cal/gm°C)

TC is total caustic as (gm/l Na_2CO_3)

Al_2O_3 is dissolved Al_2O_3 as (gm/l Al_2O_3)

T is temperature in (°C)

Source: Langa (5)

$$C_{pG} = .2694 + 6.4 \times 10^{-4} T$$

where C_{pG} is the heat capacity of gibbsite (cal/gm°C)

T is temperature in C

Source: Misra and White (1)

TABLE III

STANDARD HEAT OF FORMATION

ΔH_f [Al(OH) ₃ (c)]	:	-309.06 kcal/mole
ΔH_f [NaOH (aq)]	:	-112.36 kcal/mole
ΔH_f [NaAlO ₂ (aq)]	:	-277.0 kcal/mole
ΔH_f [H ₂ O (f)]	:	-68.31 kcal/mole

Sources: National Bureau of Standards (2), (3)
Hemmingway and Robie (4)

TABLE IV

REACTANTS AND PRODUCTS FOR SAMPLE CALCULATION

Reactants	Product
Spent Liquor at 145°C	Green Liquor at 145°C
Composition: 200 gm/l TC	Composition: 187.4 gm/l TC
60 gm/l Al_2O_3	121.8 gm/l Al_2O_3
Total Mass: 1187.7 gm*	Total Mass: 1294.9 gm
Gibbsite at 145°C	
Total Mass: 107.2 gm	

* Equivalent to the mass of one litre at 25°C.

Sample Calculation

Table IV shows the mass of gibbsite and concentration of spent and green liquor used to calculate the heat of dissolution of gibbsite. The mass of spent liquor listed is equivalent to the mass of one litre at 25°C. (The volume at 25°C is the basis for gm/l TC and gm/l Al_2O_3 concentrations.) The mass of gibbsite was chosen so that the resulting green liquor Al_2O_3/TC was .650, a typical digestion blow-off ratio. A usual Bayer digestion temperature of 145°C was chosen. With the information in Table II, III and IV and equations (2) - (7), the heat of dissolution of gibbsite can be determined at typical Bayer digestion conditions.

Step 1 - Calculate ΔH_1

$$\Delta H_1 = M_{SL} \int_{145^\circ C}^{25^\circ C} C_{pL} dT + M_G \int_{145^\circ C}^{25^\circ C} C_{pG} dT$$

Integrating the equations in Table II, using information from Table IV.

$$\int_{145^\circ C}^{25^\circ C} C_{pL} dT = -108.6 \text{ cal/gm}$$

$$\int_{145^\circ C}^{25^\circ C} C_{pG} dT = -38.856 \text{ cal/gm}$$

$$\Delta H_1 = 1187.7 \text{ gm} (-108.6 \text{ cal/gm}) + 107.2 \text{ gm} (-38.856 \text{ cal/gm})$$

$$\Delta H_1 = -133149 \text{ cal} = -133.15 \text{ kcal}$$

Step 2 - Calculate ΔH_2

$$\Delta H_2 = \Delta H_f(\text{NaAlO}_2) + 2\Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{Al}(\text{OH})_3) - \Delta H_f(\text{NaOH})$$

Using information in Table III.

$$\Delta H_2 = 7.8 \text{ kcal/mole } (\text{Al}(\text{OH})_3) = 15.6 \text{ kcal/mole } (\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O})$$

$$107.2 \text{ gm } \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} = .68727 \text{ mole } \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$$

$$\Delta H_2 = 10.72 \text{ kcal}$$

Step 3 - Calculate ΔH_3

$$\Delta H_3 = (M_{\text{SL}} + M_{\text{G}}) \int_{25^\circ\text{C}}^{145^\circ\text{C}} C_{\text{PL}} dT$$

Integrating the equation in Table II, using information from Table

IV.

$$\int_{25^\circ\text{C}}^{145^\circ\text{C}} C_{\text{PL}} dT = 105.70 \text{ cal/gm}$$

$$\Delta H_3 = 105.70 (1187.7 + 107.2) = 136.86 \text{ kcal}$$

Step 4 - Calculate ΔH_D

$$\Delta H_D = \Delta H_1 + \Delta H_2 + \Delta H_3$$

$$\Delta H_D = -133.15 + 10.72 + 136.86 = 14.43 \text{ kcal}$$

when put on an Al_2O_3 basis

$$\Delta H_D = 14.43 \frac{1}{107.2} \frac{156}{102} = 205.8 \text{ kcal/kg } \text{Al}_2\text{O}_3$$

Experimental Verification

Once the calculated value of 206 kcal/kg Al_2O_3 was determined, a search began for a method to verify the heat of dissolution of gibbsite experimentally. The experimental conditions had to be identical to those considered in the calculation, and a calorimetric method was preferred. The SETARAM C-80 heatflux calorimeter filled these prerequisites.

The SETARAM C-80 is shown in Figure 2. One C-80 feature useful in this investigation was the reversal mixing cell. The cell, shown in Figure 3, was used to keep the solid gibbsite separate from liquor until the desired temperature was reached. The cell containing separated liquor and gibbsite was placed into the calorimeter at room temperature. The cell and contents were heated and allowed to equilibrate at 145°C. Once the system reached equilibrium, the cell was inverted mixing the

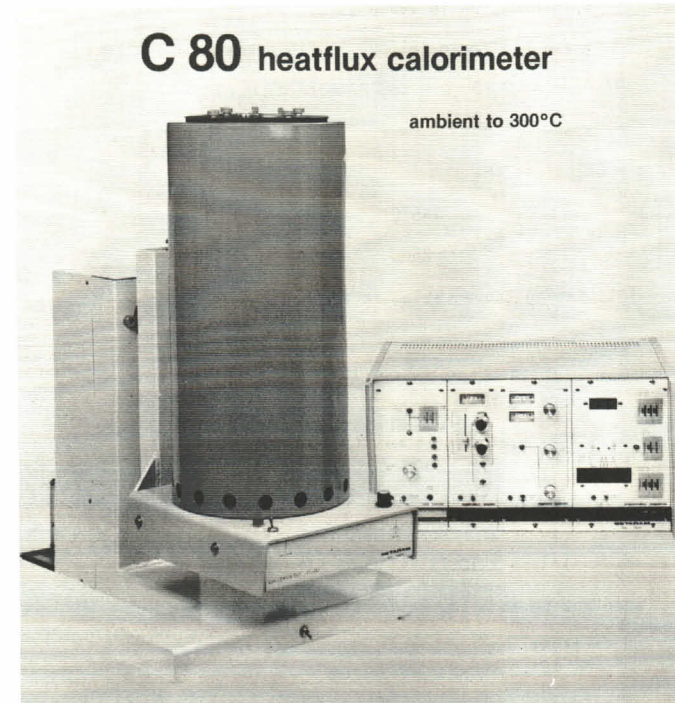


FIGURE 2. THE SETARAM C-80 HEATFLUX CALORIMETER

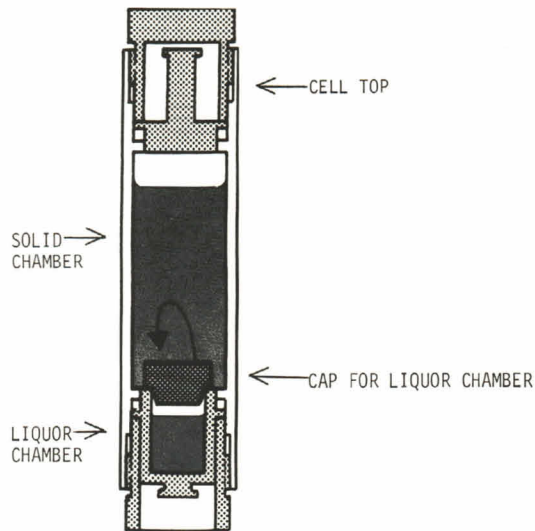


FIGURE 3. REVERSAL MIXING CELL

solid and liquid. The amount of heat required to maintain a temperature of 145°C was measured. In about one hour, the system reached a new thermal equilibrium. The total heat added to the cell to maintain 145°C less the heat added to the empty cell during calibration determined the heat of dissolution of gibbsite at 145°C.

Before any measurement of heat of dissolution was made, the SETARAM C-80 was used to measure heat capacities of pure water, a 20% NaOH solution and a synthetic Bayer liquor. The results were compared, respectively, with steam table data, caustic manufacturers heat capacities and Table II correlation for Bayer liquor heat capacity. Agreement between experimental results and literature was generally within 2%.

With confidence established in the C-80's results, three replicate experiments were run to measure the heat of dissolution of gibbsite at 145°C. All runs were made at liquor concentrations identical to those in Table IV. Because the volume of the cell (8.6 cc) was considerably smaller than the one litre basis used in the calculation, the mass of liquor and gibbsite charged was reduced proportionally.

The experimental heat of dissolution of gibbsite at 145°C was 200.9 ± 3.2 kcal/kg Al_2O_3 . The experimental value compares with the calculated value within 2.4%. This is within the accuracy of the liquor heat capacity correlation and is considered good agreement.

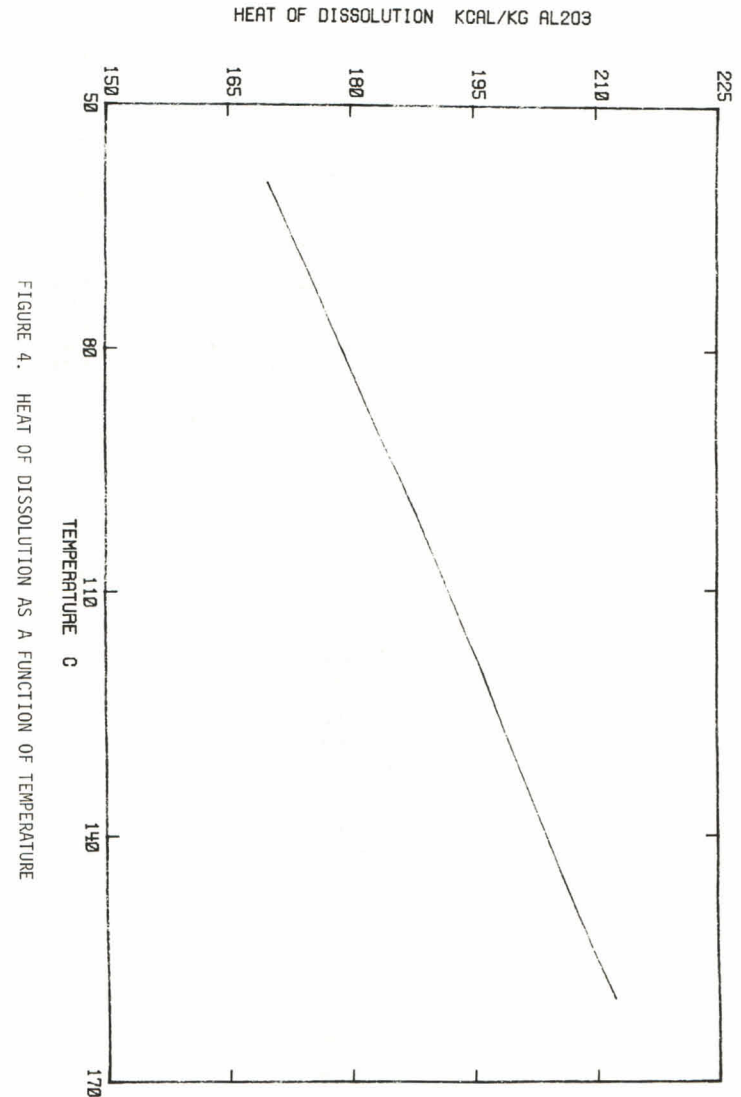


FIGURE 4. HEAT OF DISSOLUTION AS A FUNCTION OF TEMPERATURE

Conclusions

The heat of dissolution of gibbsite at Bayer digestion conditions was found to be significantly higher than the widely used values reported in the literature. An increase in heat of dissolution with temperature was found, Figure 4 shows calculated values from 60-160°C. Note that the value at 60°C, a typical precipitation temperature, is higher than the average Table I value, but compares well with the value reported by Adamson.

Heats of dissolution of gibbsite as calculated by the previously outlined procedure have been used in hand calculations and in a steady state computer model for digestion. Agreement between calculated steam usage and process temperatures and those observed in plant operation has greatly improved.

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