

## KINETICS OF AMMONIA RECOVERY FROM SODA-PLANT LIQUOR BY BURNT MAGNESITE

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Received July 14th, 1987  
Accepted December 17th, 1987

The kinetics of the reaction of a soda-plant liquor containing ammonium chloride and sodium chloride with softly burnt magnesite have been investigated using a modified distillation test. Evaluation of the kinetic data has shown that the reaction rate is controlled by the dissolution of the solid phase. The kinetic equation for this variant of reaction mechanism has been modified to obtain a form suitable for chemical engineering calculations. A procedure of determining the adjustable parameters of this equation is illustrated by treating the obtained experimental data.

Our previous paper<sup>1</sup> has given the results of a kinetic study on the reaction of an ammonium chloride solution with pure magnesium oxide in the form of small, non-porous particles. An assessment of the measurements and of the evaluation results has indicated that the slowest process from the macrokinetic point of view is the dissolution of the solid phase. The following equation has been proposed to describe the reaction kinetics:

$$r_{BS} = k_5 \{ S_B - c_{Mg^{2+}} [ S_Z c_{NH_3} / (K_1 c_{NH_4} + c_{H_2O}) ]^2 \}, \quad (1)$$

where  $r_{BS}$  is the rate of MgO removal per unit interface area,  $\text{mol m}^{-2} \text{s}^{-1}$ ,  $k_5$  is the rate constant for  $\text{Mg}(\text{OH})_2$  precipitation,  $\text{mol}^{-2} \text{m}^{10} \text{s}^{-1}$ ,  $S_B$  is the solubility product of  $\text{Mg}(\text{OH})_2$ ,  $\text{mol}^3 \text{m}^{-12}$ ,  $S_Z$  is the ionic product of water,  $\text{mol}^2 \text{m}^{-6}$ ,  $K_1$  is the equilibrium constant of  $\text{NH}_4\text{Cl}$  hydrolysis, and  $c_i$  is the concentration of  $i$ -th component,  $\text{mol m}^{-3}$ .

As a continuation of the previous study, the present communication illustrates how values of the quantities appearing in the kinetic equation can be obtained, thus establishing the requirement for the use of the equation in chemical engineering calculations.

### EXPERIMENTAL

The reaction kinetics were followed in an apparatus shown in Fig. 1 by monitoring the amount of ammonia desorbed from a suspension of MgO in an aqueous salt solution at the boiling

point. The liberated ammonia together with condensed water vapour were collected in a receiver containing a known amount of  $\text{H}_2\text{SO}_4$ . The time for the given amount of  $\text{H}_2\text{SO}_4$  to neutralize was determined by means of an indicator. When the end point was reached, a further dose of the acid was added to the receiver. The receiver consisted of a calibrated vessel, so that the amount of the condensate introduced could be followed simultaneously. In order to prevent changes in the solution concentration due to evaporation, the same amount of water as leaving in the form of vapour was continuously supplied to the reactor. The addition of 10 g of ground (320) corundum enhanced the ammonia desorption from the liquid phase by increasing markedly the number of water vapour bubbles. The time lag between the liberation of ammonia from the suspension and its absorption in the receiver was reduced by passing air through the apparatus. The result of the measurements was the dependence of MgO conversion on the reaction time.

The experiments were carried out with a solution obtained by dissolving salts of analytical grade (Lachema) in distilled water, and with calcined magnesite containing 80.3 mass % of active MgO. Its specific surface area, as determined by the comparative dynamic method using adsorption of nitrogen from a nitrogen-hydrogen mixture at the temperature of liquid nitrogen, was  $40 \text{ m}^2 \text{ g}^{-1}$ . The measurements were performed with a 50-fold excess of  $\text{NH}_4\text{Cl}$  beyond stoichiometry.

## RESULTS AND DISCUSSION

In describing the kinetics, the reaction rate is usually expressed per unit volume of the reaction space. This quantity is related to  $r_{\text{BS}}$  by

$$r_{\text{BV}} = -(1/V)(dn_{\text{B}}/d\tau) = S_{\text{V}}r_{\text{BS}}, \quad (2)$$

where  $r_{\text{BV}}$  is the reaction rate per unit volume of reactor,  $\text{mol m}^{-3} \text{ s}^{-1}$ ,  $V$  is the reactor volume,  $\text{m}^3$ ,  $n_{\text{B}}$  is the number of moles of MgO in the reactor during the reaction, mol,  $\tau$  is the reaction time, s, and  $S_{\text{V}}$  is the surface area of MgO per unit volume of reactor at a given instant of the reaction,  $\text{m}^{-1}$ .

Let us consider a magnesium feedstock whose MgO content is specified by the mass fraction, and suppose that the contribution of MgO to the total solid phase surface area is proportional to its mass fraction, both in the starting material and in the solid phase during the reaction. The surface area of MgO per unit volume of

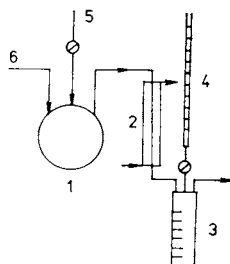


FIG. 1

Apparatus. 1 boiling flask, 2 condenser, 3 receiver, 4 burette with  $\text{H}_2\text{SO}_4$ , 5 water supply, and 6 air inlet

reactor at reaction time  $\tau$  is then given by

$$S_V = GwS/V, \quad (3)$$

where  $G$  is the mass of the solid phase during the reaction,  $g$ ,  $w$  is the mass fraction of MgO in the solid phase at a given instant, and  $S$  is the specific surface area of the solid phase at a given instant of the reaction,  $\text{m}^2 \text{g}^{-1}$ .

The mass balance for the solid phase during its reaction gives the following expression:

$$G = G^0 - (G_B^0 - G_B) = G^0(1 - w^0\eta_B), \quad (4)$$

where  $G^0$  and  $G_B^0$  are the masses of the solid phase and MgO entering the reactor,  $g$ , respectively,  $w^0$  is the mass fraction of MgO in the magnesium feedstock, and  $\eta_B$  is the MgO conversion.

Using Eq. (4) and a relation between the mass and conversion of MgO in the reactor,

$$G_B = G_B^0(1 - \eta_B) = G^0w^0(1 - \eta_B), \quad (5)$$

we arrive at the following expression for the instantaneous mass fraction of MgO in the solid phase

$$w = G_B/G = w^0(1 - \eta_B)/(1 - w^0\eta_B). \quad (6)$$

Let us define a function  $f_S$  that characterizes the variation in the specific surface area of the solid phase during the reaction:

$$f_S = S/S^0. \quad (7)$$

Inserting Eqs (7), (4) and (6) into (3), we obtain

$$S_V = G^0w^0S^0f_S(1 - \eta_B)/V. \quad (8)$$

Substitution of the balance equation

$$n_B = n_B^0(1 - \eta_B) = G^0w^0(1 - \eta_B)/M_B, \quad (9)$$

where  $n_B^0$  is the number of moles of MgO entering the reactor, mol, and  $M_B$  is the molar mass of MgO,  $\text{g mol}^{-1}$ , kinetic equation (1) and Eq. (8) in Eq. (2) and rearrangement give

$$(d\eta_B/d\tau) = k_5 M_B S^0 f_S \{ S_B - c_{Mg}^2 + [S_Z c_{NH_3} / (K_1 c_{NH_4} + c_{H_2O})]^2 \} (1 - \eta_B). \quad (10)$$

This equation describes the reaction kinetics for both burnt magnesite and pure MgO, as can be seen from comparison with the equation for the pure component derived in our previous paper<sup>1</sup>.

If the knowledge of the decomposition of NH<sub>4</sub>Cl is more important, then it is convenient to describe the reaction kinetics in terms of NH<sub>4</sub>Cl conversion. Let us suppose that the reaction is carried out with an excess of MgO beyond stoichiometry, and define the excess by

$$P = an_{\text{B}}^0/(bn_{\text{A}}^0) = 2n_{\text{B}}^0/n_{\text{A}}^0, \quad (11)$$

where  $P$  is the excess of MgO over the stoichiometric amount,  $a$  and  $b$  are the stoichiometric coefficients for NH<sub>4</sub>Cl and MgO, respectively, and  $n_{\text{A}}^0$  is the number of moles of NH<sub>4</sub>Cl entering the reactor. If NH<sub>4</sub>Cl is the key component, then the number of moles of MgO in the reactor during the reaction can be described by the balance equation

$$n_{\text{B}} = n_{\text{B}}^0 - bn_{\text{A}}^0\eta_{\text{A}}/a. \quad (12)$$

By combining Eqs (12) and (9), we obtain

$$\eta_{\text{A}} = P\eta_{\text{B}}. \quad (13)$$

Denoting the expression within braces in Eq. (10) by the symbol  $h$ , and substituting (13) in (10), we can rewrite Eq. (10) in the form

$$(d\eta_{\text{A}}/d\tau) = k_5 M_{\text{B}} S^0 P f_s h (1 - \eta_{\text{A}}/P), \quad (14)$$

where  $h$  is the driving force for the reaction, mol<sup>3</sup> m<sup>-12</sup>. This equation describes the reaction kinetics for NH<sub>4</sub>Cl as the key component.

A series of preliminary measurements have been carried out in order to see if the conclusion made in our previous study<sup>1</sup> for MgO also applies to magnesium feedstock prepared by magnesite calcination. It has been found that the addition of 10 g of ground corundum to 200 ml of solution enhances ammonia desorption to the extent that this process no longer controls the overall reaction rate. It has also been confirmed that the reaction rate does not depend on whether MgO was hydrated before use. Measurements performed with calcined magnesite of various particle sizes have shown that for grains smaller than 0.3 mm, the decelerating effect of transport processes within the porous structure is no longer of importance. Also, the values of  $(d\eta_{\text{B}}/d\tau)$  observed at the onset of the reaction exhibited only a slightly increasing trend with increasing NH<sub>4</sub>Cl concentration in the starting solution,  $c_{\text{A}}^0$ , mol m<sup>-3</sup> (Fig. 2), in accord with Eq. (10) reduced for this case to the form

$$(d\eta_{\text{B}}/d\tau)_{\tau \rightarrow 0} = k_5 M_{\text{B}} S^0 S_{\text{B}}. \quad (15)$$

This increase may be explained by changes in the solubility product of  $\text{Mg}(\text{OH})_2$ . Thus, the results obtained for burnt magnesite have shown that, when grains smaller than 0.3 mm are used and ammonia desorption is rapid, the dissolution of the solid phase becomes the rate-controlling step. Under these conditions, the decomposition kinetics can be described by the same equation as derived for pure  $\text{MgO}$  in the form of nonporous particles.

Apparently, the dependence of the quantity  $(d\eta_B/d\tau)_{\tau \rightarrow 0}$  on  $c_A^0$  cannot be expected to be linear for very dilute solutions. Nevertheless, the relatively small slope of the linear plot for  $c_A^0 \geq 3.8 \cdot 10^2 \text{ mol m}^{-3}$  (see Fig. 2) does permit the rate constant  $k_5$  to be estimated. For the value of  $(d\eta_B/d\tau)_{\tau \rightarrow 0}$  obtained by extrapolation to  $c_A^0 = 0$ , the solubility product of  $\text{Mg}(\text{OH})_2$  assumes a value equal to that of water. On the basis of literature data<sup>2</sup>, the dependence of this quantity on temperature can be expressed as

$$S_B = 1.33 \cdot 10^{-4}(178 - t). \quad (16)$$

Using the value of  $S_B$  at the temperature of measurement and the specific surface area of the solid phase, the rate constant  $k_5$  was calculated as  $8.53 \cdot 10^{-5}$ . Assuming that this quantity is dependent on temperature only and that the effect of the non-ideality of solution at higher salt concentrations is included with the other adjustable parameters of the kinetic equation, the rate constant can be used to determine values of  $S_B$  for  $\text{NH}_4\text{Cl}$  solutions of various concentrations.

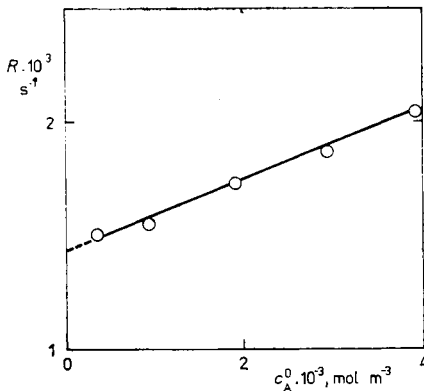


FIG. 2

Effect of the concentration of  $\text{NH}_4\text{Cl}$  solution on the value of  $R(\equiv (d\eta_B/d\tau)_{\tau \rightarrow 0})$ ,  $P = 0.02$

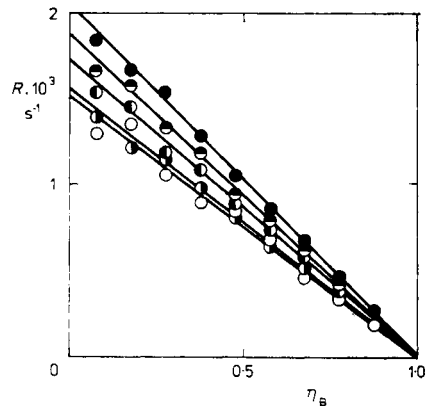


FIG. 3

Reactions isotherms for various concentrations of  $\text{NH}_4\text{Cl}$  solution.  $R(\equiv (d\eta_B/d\tau)_{\tau \rightarrow 0})$ ,  $P = 0.02$ ;  $c_A^0 \cdot 10^{-3} \text{ mol m}^{-3}$ :  $\circ$  0.38,  $\bullet$  0.95,  $\circ$  1.92,  $\bullet$  2.95,  $\bullet$  3.95

In this way, the following expression has been obtained from experimental data or the dependence of  $S_B$  on the concentration of  $\text{NH}_4\text{Cl}$  in the starting solution:

$$S_B = 1.04 \cdot 10^{-2} + 1.12 \cdot 10^{-6} c_A^0 \quad (17)$$

On the basis of so obtained data and decomposition isotherms measured at a large excess of  $\text{NH}_4\text{Cl}$  beyond stoichiometry, where it is reasonable to assume that the solution composition varies very little during the decomposition and hence the solubility product of  $\text{Mg}(\text{OH})_2$  remains invariant in the course of the reaction, it is possible to calculate the variation in the specific surface area of the solid phase with conversion  $\eta_B$ , i.e., to determine the function  $f_S$ . Using the reaction isotherms shown in Fig. 3, we found that the function  $f_S$  does not change with increasing conversion of  $\text{MgO}$  over the whole range of  $\text{NH}_4\text{Cl}$  concentrations investigated, remaining in all cases at a value of 1.

If the decomposition is carried out at a  $\text{NH}_4\text{Cl}$  to  $\text{MgO}$  ratio close to the stoichiometric one, then the  $\text{NH}_4\text{Cl}$  content decreases and the amount of  $\text{MgCl}_2$  increases during the course of the reaction; as the solution composition changes, the value of  $S_B$  also changes. From the practical point of view, it is therefore advantageous to determine the magnitude of the driving force for the reaction, i.e., the value of the term within braces in Eq. (10), for a given phase of the decomposition. For this

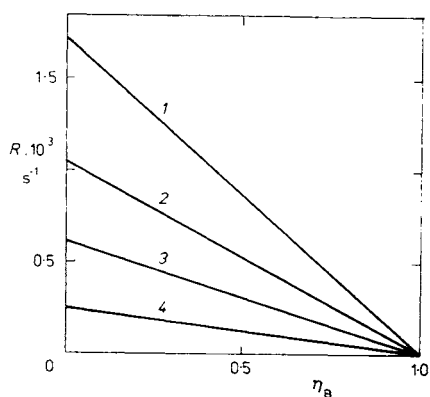


FIG. 4

Reaction isotherms for  $\text{NH}_4\text{Cl}$  solutions which have been reacted to various conversion.  $R \equiv (d\eta_B/d\tau)_{\tau \rightarrow 0}$ ,  $c_A^0 = 3.95 \cdot 10^3 \text{ mol} \cdot \text{m}^{-3}$ ,  $P = 0.02$ ,  $\eta_A$ : 1 0.25, 2 0.50, 3 0.85, 4 0.95

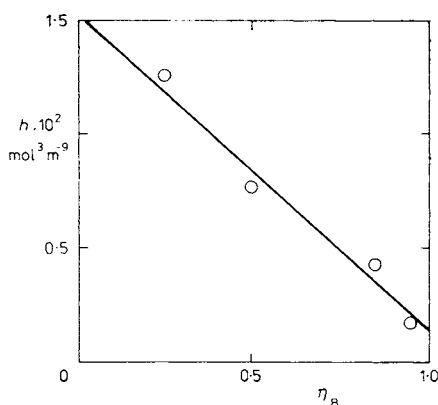


FIG. 5

A plot of the driving force for the reaction against  $\text{NH}_4\text{Cl}$  conversion.  $c_A^0 = 3.95 \cdot 10^3 \text{ mol} \cdot \text{m}^{-3}$ ,  $P = 1.1$

purpose, it is convenient to use reaction isotherms obtained at a large excess of solutions which have reacted to some extent (Fig. 4). When the liquid phase is at a large excess, the change in the solution composition is sufficiently small to be negligible. The driving force therefore remains constant throughout the decomposition, and the reaction rate changes only as a result of the reduction in the MgO surface area. The average values of the driving force calculated for a solution with an initial concentration of  $3.95 \cdot 10^3 \text{ mol m}^{-3} \text{ NH}_4\text{Cl}$  at  $P = 1.1$  are plotted as a function of  $\text{NH}_4\text{Cl}$  conversion in Fig. 5. The obtained linear dependence can be represented by the equation

$$h = h^0(1 - \eta_A/P), \quad (18)$$

where  $h^0$  is the driving force for the reaction at  $\tau \rightarrow 0$ ,  $\text{mol}^3 \text{ m}^{-1.2}$ . For the given case,  $h^0$  was found to be  $1.52 \cdot 10^{-2} \text{ mol}^3 \text{ m}^{-1.2}$ . Since the origin of the straight line, which corresponds to zero conversion, is determined by the solubility product of  $\text{Mg}(\text{OH})_2$  in the starting  $\text{NH}_4\text{Cl}$  solution of a given concentration, it is possible to construct the plots for solutions of other concentrations which have not been measured.

Since the effect of NaCl at concentrations at which it occurs in the soda-plant liquor has been found to be insignificant, the results obtained are sufficient for the determination of the shape of the decomposition isotherm and can be used as input data in chemical engineering calculations. For this purpose, it is useful to convert kinetic equation (1), by applying a relationship between the reaction rates for  $\text{NH}_4\text{Cl}$  and MgO obtained from the stoichiometric equation and with the use of Eqs (2), (8), (13) and (18), into the form

$$r_{\text{AV}} = 2k_5 G^0 w^0 S^0 h^0 f_S (1 - \eta_A/P)^2 / V, \quad (19)$$

where  $r_{\text{AV}}$  is the rate of removal of  $\text{NH}_4\text{Cl}$  per unit volume of reactor,  $\text{mol m}^{-3} \text{ s}^{-1}$ .

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Translated by M. Škubalová.