

# Special Feature: Advanced Thermal Management Technology for Developing the High-efficiency Vehicle

Research Report

## Reaction Kinetics of Ammonia Absorption/Desorption of Metal Salts

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Report received on Jun. 19, 2018

**■ABSTRACT■** The reversible reactions between ammine magnesium complex and ammonia are studied by volumetric method and the heterogeneous reaction kinetic analysis at a grain level. The influence of heat and mass transfer limitations at a pellet level on the overall absorption/desorption rate is sufficiently minimized with the reactive block and the micro-channel reactor. The pseudo equilibrium for  $\text{Mg}(\text{NH}_3)_2\text{Cl}_2 + 4\text{NH}_3 \leftrightarrow \text{Mg}(\text{NH}_3)_6\text{Cl}_2$  is not observed in the volumetric measurement. The kinetic parameters for the kinetic model are identified by the experimental data. The analysis reveals that the heterogeneous temperature or pressure distribution in the grain is the predominant factor on the overall absorption/desorption rate.

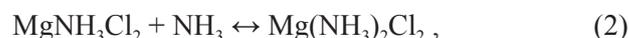
**■KEYWORDS■** Chemical Heat Pump, Reaction Kinetics, Gas-solid Reaction, Ammine Magnesium Complex

### 1. Introduction

Solid-gas reversible reactions between metal chloride and ammonia have a great potential to recover waste heat in intermediate temperature range from 100 to 200°C. The combination of metal chloride and ammonia is suitable for waste heat recovery systems such as chemical heat pumps in terms of the environmental load and availability.

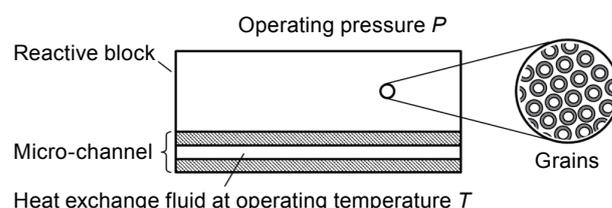
Metal chlorides and ammonia reactions have widely been investigated on the thermodynamic equilibrium characteristics<sup>(1-3)</sup> and the reaction kinetics.<sup>(4-8)</sup> The performance of the solid-gas reaction system is subject to the heat and mass transfer limitations. The temperature difference between the metal salt and the ammonia gas due to the poor heat exchange capability results in the pseudo equilibrium.<sup>(1,9)</sup> The graphite-metal salt composite block<sup>(5,10)</sup> is a promising solution to enhance the apparent thermal conductivity.

Magnesium chloride is a favorable material for waste heat recovery at intermediate temperature. The magnesium chloride and ammonia reversible reaction formulae are as follows:



The reaction of the Eq. (3) is well-suited in terms of the thermodynamic equilibrium.<sup>(1,2)</sup> However, pseudo equilibrium behavior was observed for the same reason mentioned above. A reliable measurement of thermodynamic properties is demanded for system design.

Development of a practical kinetic model for solid-gas heterogeneous reactions is of importance to predict heat recovery system performance at various operating conditions. The grain-pellet concept as shown in **Fig. 1**



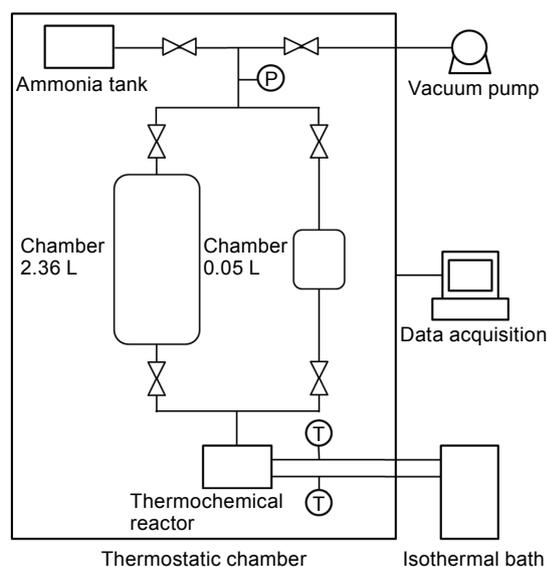
**Fig. 1** Illustration of the grain-pellet concept.

is applied to couple heat and mass transfer with chemical reaction at micro/macrosopic scales.<sup>(4-8)</sup> The grain refers to a microscopic basic particle while the pellet represents a reactive block with metal salt.

In this study, reactions between ammine magnesium complex and ammonia including the influence of heat and mass transfer on the overall absorption/desorption rate were investigated. The volumetric measurements were conducted to obtain the thermal dynamic properties and the reaction rate at various pressures and temperatures. In addition, the absorption/desorption processes were analyzed by solid-gas heterogeneous reaction models at the grain level.

## 2. Experimental Set-up

The schematic illustration of the experimental set-up for the volumetric measurements is shown in **Fig. 2**. The experimental apparatus consisted of a thermochemical reactor with micro-channels, two gas chambers with different sizes, an ammonia tank, a vacuum pump, a thermostatic chamber and an isothermal bath. Molded  $MgCl_2$  blocks were loaded into the thermochemical reactor. The equilibrium pressure measurements were performed with the small gas chamber to enhance the measurement sensibility. The small chamber also allows us to set large initial pressure difference between operation pressure and equilibrium pressure to enhance the diffusion of ammonia gas in the reactive



**Fig. 2** Schematic of the experimental set-up.

block/grain. Also, reaction rates were measured by use of the large gas chamber to minimize pressure change during the measurements.

The preparation of the  $MgCl_2$  blocks was conducted in a dry room to prevent  $MgCl_2$  from being hydrated. Anhydrous magnesium chloride powder supplied by SIGMA ALDRICH was used. Carbon fibers were mixed with anhydrous magnesium as a thermally-conductive filler. The diameter and length of the carbon fibers were 10  $\mu m$  and 200  $\mu m$ , respectively. The filling amount of the carbon fibers was 30 vol%. The mixture of anhydrous magnesium chloride and the carbon fiber was poured into a mold which was 15 mm square and molded by a hand press. The crystalline state of the grain was identified as anhydrous magnesium chloride by X-ray diffraction after these procedures. The reactive block was loaded into the reactor and heated up to 443 K in a vacuum. The apparent thermal conductivity of the reactive block was more than 3 W/(m·K).

The system temperature was controlled at 318 K by the thermostatic chamber so that ammonia gas did not condense on the gas chamber wall while the thermochemical reactor temperature was independently regulated in the range of 333 K from 448 K by the isothermal bath.

A thermogravimetric (TG) measurement system with a magnetic suspension balance (MCB-CP-MP-250, MSB-VG-S2, BEL JAPAN, INC.) was employed for data comparison. Seven milligrams of magnesium chloride powder was loaded into a stainless basket. The basket was in a closed vessel heated by an isothermal bath. The vessel was evacuated by a vacuum pump at 453 K for 6 hours before thermodynamic equilibrium measurement.

## 3. Volumetric Method

Absorption/desorption amount was obtained by the change of pressure in the volumetric method. The gas pressure was measured by a capacitance manometer in the present apparatus. The number of moles in the gas chamber was calculated by the Soave-Redlich-Kwong equation:

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)}, \quad (4)$$

$$a = \frac{0.427R^2T_c^2}{P_c}, \quad (5)$$

$$b = \frac{0.0866 RT_c}{P_c}, \quad (6)$$

$$\alpha = \left(1 + 0.863 \left(1 - (T/T_c)^{0.5}\right)\right)^2, \quad (7)$$

where  $P$  is gas pressure,  $P_c$  critical pressure,  $V$  molar volume,  $R$  gas constant,  $T$  salt temperature, and  $T_c$  critical temperature. The molar ratio  $x$  and the reaction rate are defined as follows:

$$x = \frac{n_{\text{MgCl}_2 \cdot 6\text{NH}_3}}{n_{\text{MgCl}_2 \cdot 2\text{NH}_3} + n_{\text{MgCl}_2 \cdot 6\text{NH}_3}} \quad \text{for absorption}, \quad (8)$$

$$x = \frac{n_{\text{MgCl}_2 \cdot 2\text{NH}_3}}{n_{\text{MgCl}_2 \cdot 2\text{NH}_3} + n_{\text{MgCl}_2 \cdot 6\text{NH}_3}} \quad \text{for desorption}, \quad (9)$$

$$\frac{dx}{dt} \approx \frac{x_{t+\Delta t} - x_t}{\Delta t}, \quad (10)$$

where  $n$  is the molar number of the substance,  $t$  time, and  $\Delta t$  the sampling time.

#### 4. Thermodynamic Equilibrium

Thermodynamic equilibrium of solid-gas reaction is represented by the Clausius-Clapeyron equation:

$$\ln(P_{\text{eq}}/P_0) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}, \quad (11)$$

where  $P_{\text{eq}}$  is the equilibrium pressure,  $P_0$  the atmospheric pressure,  $\Delta H$  the enthalpy change, and  $\Delta S$  entropy change, respectively.

#### 5. Reaction Kinetics

Kinetic models of the heterogeneous reaction in the grain scale are discussed here. It was assumed that macroscopic heat and mass transfer did not dominate the overall reaction rate since the apparent heat conductivity and gas permeability of the reaction block were highly enhanced.

The semi-empirical kinetic model proposed by Mazet et al.<sup>(6)</sup> for absorption/desorption rate as a function of the molar ratio  $x$ ,  $P$  and  $T$  was adopted here:

$$dx/dt = f(x) \cdot k(P, T). \quad (12)$$

The right hand side of the Eq. (12) consists of two components. The commonly-used form for the  $f(x)$  term is as follows:

$$f(x) = (1-x)^m, \quad (13)$$

where  $m$  is the pseudo-order of the reaction to be identified. The value of  $m$  is in the range of 0-2 with no physical meaning. The  $k(P, T)$  term is the specific rate of the heterogeneous reaction:

$$k(P, T) = s \exp(-E_a/RT) \cdot g(P, T) = Ar \cdot g(P, T), \quad (14)$$

where  $s$  is pre-exponential factor,  $E_a$  the activation energy. The Arrhenius term  $Ar$  is weighted the  $g(P, T)$  term to express the thermodynamic equilibrium drop due to the heterogeneous reaction at the grain. The power functions  $g(P, T) = [(P - P_{\text{eq}}(T))/P_{\text{eq}}(T)]^n$  for absorption,  $g(P, T) = [(P_{\text{eq}} - P(T))/P_{\text{eq}}(T)]^n$  for desorption were selected to allow greater flexibility for the model development although there are various expressions for  $g(P, T)$  such as  $(P - P_{\text{eq}}(T))/P_{\text{eq}}(T)$  and  $\ln[P/P_{\text{eq}}(T)]$ . The equilibrium pressure  $P_{\text{eq}}(T)$  is estimated by the Clausius-Clapeyron Eq. (11). Thus,  $s$ ,  $E_a$ ,  $m$ ,  $n$  are the parameters to be experimentally identified.

#### 6. Result and Discussion

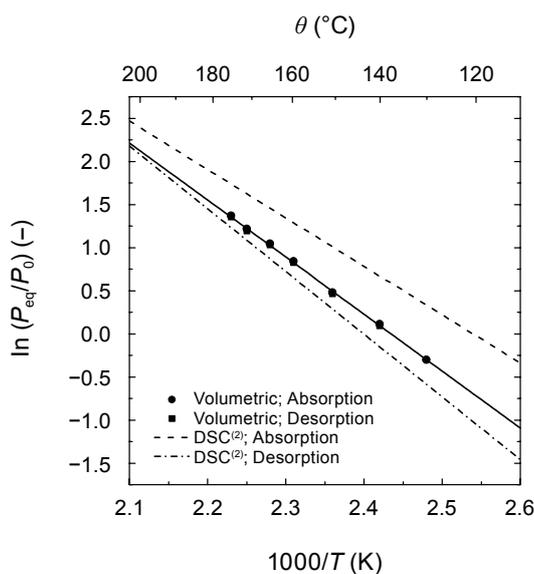
**Figure 3** shows the dependency of the average absorption rates on the thickness of the reactive block to demonstrate the validity of the assumption that macroscopic heat and mass transfer limitations were sufficiently small. The average absorption rate was calculated by the time required for the reactive block to absorb 90% of the total absorption amount. The reactive blocks with 1.2, 1.5, 1.75, 2.0, 2.5 and 3.0 mm thick were used. The initial gas pressure  $P_{\text{init}}$  was 600 kPa, the salt temperature  $T$  was 403 K. The average absorption rate increased as the reactive block thickness decreased in the range of the reactive block thickness from 3.0 mm to 1.5 mm. Further enhancement of the absorption rate was not observed at 1.2 mm. Thus, from here on, all results were obtained by use of the reactive block of 1.2 mm thick.

The thermal equilibrium of  $\text{Mg}(\text{NH}_3)_2\text{Cl}_2 + 4\text{NH}_3$



shows typical examples of the absorption/desorption rates at various pressure. Mazet et al. has reported the great dependence of reaction rate against the pressure as to manganese chloride.<sup>(6)</sup> Also, absorption was significantly slow for the small pressure difference at the initial stage. This phenomenon could cause the pseudo equilibrium behavior in the TG measurement. The absorption in the initial stage was accelerated by large pressure difference.

**Figure 8** shows the dependency of absorption/desorption rate at  $x = 0.5$  on  $(P - P_{eq})/P_{eq}$  or  $(P_{eq} - P)/P_{eq}$ . The power functions fitted well for both absorption and desorption. The pre-exponential factors and activation energies were estimated by the Arrhenius plots in **Fig. 9**. The values of the kinetic parameters identified by experimental results in the range of  $0.25 < x < 0.9$  at various conditions on pressure and temperature are shown in **Table 2**.



**Fig. 6** Clausius-Clapeyron diagram for  $Mg(NH_3)_2Cl_2 + 4NH_3 \leftrightarrow Mg(NH_3)_6Cl_2$ .

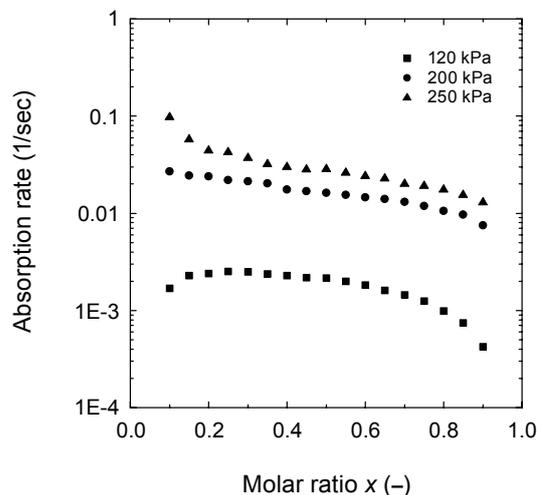
**Table 1** Enthalpy and entropy changes for the reactions.

|                                | $\Delta H$ (kJ/mol) | $\Delta S$ (J/(Kmol)) |
|--------------------------------|---------------------|-----------------------|
| Volumetric method              | 55.0                | 133.9                 |
| DSC; Absorption <sup>(2)</sup> | 46.7                | 118.5                 |
| DSC; Desorption <sup>(2)</sup> | 60.5                | 145.1                 |

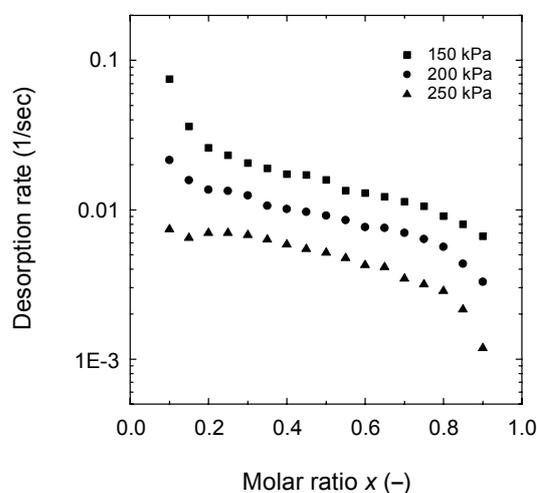
Time advancements of absorption and desorption under various pressure are shown in **Fig. 10**. The kinetic model predicted the experimental data variation well in wide pressure range. However, the predictions by the kinetic model slightly overestimate the absorption/desorption rates for small pressure difference conditions. The phenomena which absorption/desorption become very slow in the initial stage with small pressure difference should be taken into account for a better prediction.

The time required for absorption/desorption was predicted by the present kinetic model as a function of pressure and temperature as shown in **Fig. 11**. The thick line indicates the equilibrium line. The picture

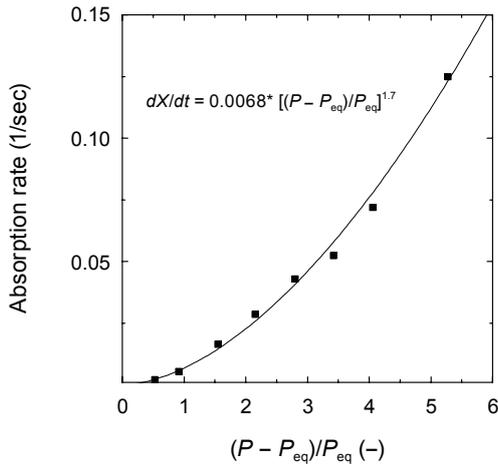
(a) Absorption;  $T = 403$  K,  $P_{init} = 120, 200, 350$  kPa



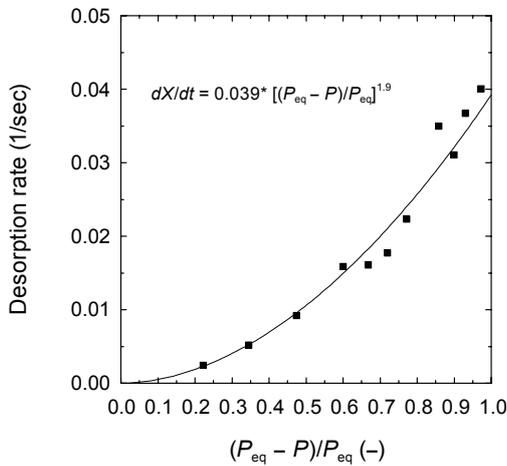
(b) Desorption;  $T = 443$  K,  $P_{init} = 150, 200, 250$  kPa



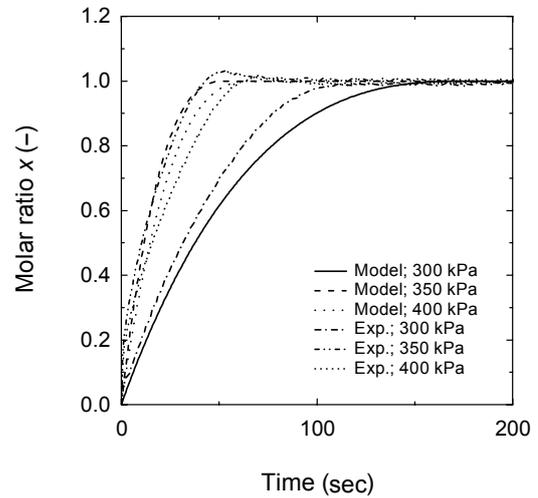
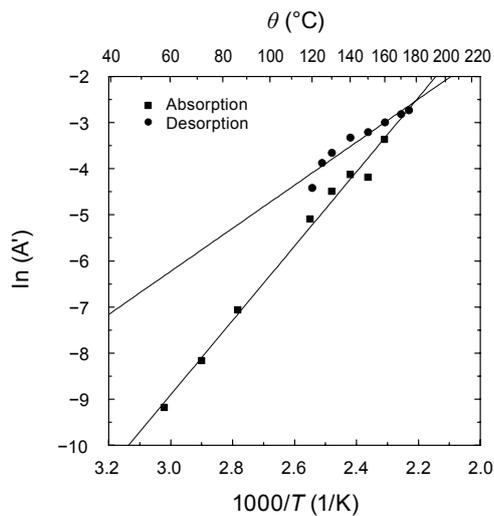
**Fig. 7** Dependency of the reaction rate on  $x, P$ .

(a) Absorption,  $T = 403$  K,  $x = 0.5$ **Table 2** Kinetic parameters.

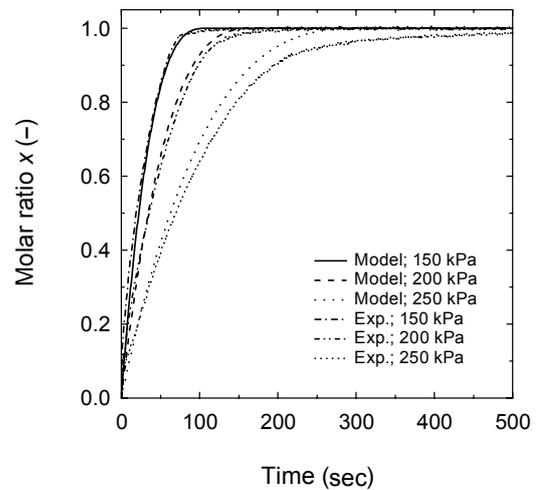
|            | $s$ [1/sec]        | $E_a$ [kJ/mol] | $m$  | $n$ |
|------------|--------------------|----------------|------|-----|
| Absorption | $4.31 \times 10^6$ | 67.0           | 0.65 | 1.7 |
| Desorption | $2.41 \times 10^3$ | 38.8           | 0.67 | 1.9 |

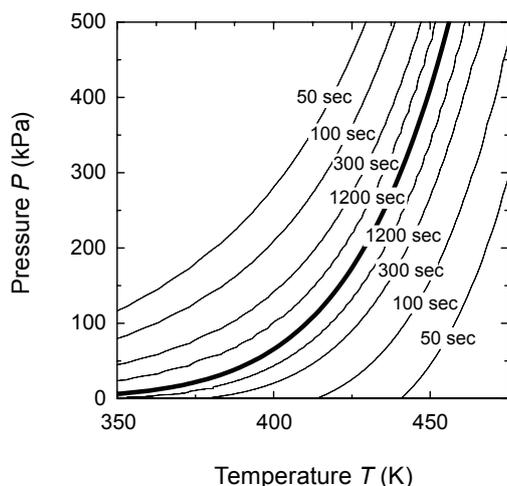
(b) Desorption,  $T = 448$  K,  $x = 0.5$ 

(a) Absorption; 423 K

**Fig. 8** Determination of the exponents in  $g(P, T)$ 

(b) Desorption; 448 K

**Fig. 9** Arrhenius plots for  $Mg(NH_3)_2Cl_2 + 4NH_3 \leftrightarrow Mg(NH_3)_6Cl_2$ .**Fig. 10** Time advancement of absorption/desorption for various pressure.



**Fig. 11** The time required for absorption/desorption; thick line: equilibrium line.

clarifies the influence of the pressure difference on the absorption/desorption rate under the conditions in which heat and mass transfer limitations are minimized.

## 7. Conclusion

The thermal equilibrium pressures and the overall absorption/desorption rate of  $\text{Mg}(\text{NH}_3)_2\text{Cl}_2 + 4\text{NH}_3 \leftrightarrow \text{Mg}(\text{NH}_3)_6\text{Cl}_2 + 4\Delta H$  were measured by the volumetric method. The volumetric measurement system allowed us to evaluate thermodynamic property of ammine magnesium complex without pseudo equilibrium behavior. The results indicate that the temperature and pressure distributions in the pellet/grain result in pseudo equilibrium behavior. Large initial pressure differences between equilibrium pressure and operation pressure were required to enhance absorption/desorption and to measure equilibrium pressure in practical measurement times.

The kinetic parameters for the heterogeneous kinetic model at the grain level were determined. The prediction by the present kinetic model agreed well with experimental data over the wide range of pressure. The kinetic model will be helpful for practical system designs.

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