Non-equilibrium sorption performances for composite sorbents of chlorides - ammonia working pairs for refrigeration

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Abstract: The sorption/ desorption characteristics under the non-equilibrium conditions are extremely important for the refrigeration. The experimental test unit is set up, and the p - T - x curves of different working pairs are tested under the non-equilibrium working conditions. The results show that non-equilibrium sorption/ desorption processes are related with dual variables rather than a single variable. Then we tested the isobaric sorption/ desorption processes of chlorides. Results show that the hysteresis phenomena are related with the desorption enthalpy. Sorption/ desorption dynamic models are studied. For sorption process the model is in accord with D-A equation, but for the desorption process both D-A equation and Spinner model should be considered. The Arrhenius equation is used to fit the relation between reaction heat and desorption hysteresis. The results show that the non-equilibrium equations fit the refrigeration performance well, whereas the theoretical equilibrium curves have big error.

Key words: Non-equilibrium condition; Sorption/ desorption; Working pair; Hysteresis; Kinetic model

Nomenclature

$a, b, c_1, c_2, c_3, i, m,$ and n Reaction equilibrium coefficients.

A Frequency factor

A_e The effective area of cross section of ammonia in the evaporator/ condenser (m^2)

c Specific heat ($\text{kJ kg}^{-1}\text{K}^{-1}$)

E Activation energy (kJ mol^{-1})

g Gravity acceleration (m s^{-2})

H Enthalpy (kJ mol^{-1})

k, n Constants for D-A equation

K constant in Arrhenius equation

L Latent heat (kJ kg^{-1})

m Sorbent mass (kg)

M Metal element

p Pressure (Pa)

Q Energy (kW)

r Velocity

R Gas constant ($\text{kJ mol}^{-1}\text{K}^{-1}$)

S Entropy ($\text{kJ mol}^{-1}\text{K}^{-1}$)

t Time (s)

T Temperature (K)

v' Specific volume of saturated liquid ($\text{m}^3 \text{kg}^{-1}$)

v'' Specific volume of saturated vapor ($\text{m}^3 \text{kg}^{-1}$)

x Sorption quantity (kg kg^{-1})

x_0 Maximum sorption quantity (kg kg^{-1})

Greek letters

ΔH Reaction enthalpy (kJ mol^{-1})

Δp Pressure difference between the two ends of ammonia column (Pa)

$\Delta(\Delta p)$ Difference between the data in sorption/desorption process and the initial data (Pa)

ΔS Reaction entropy ($\text{kJ mol}^{-1}\text{K}^{-1}$)

ΔV The volume change in adsorption/desorption process (m^3)

Δx Cycle sorption quantity (kg kg^{-1})

Subscripts

am/ NH_3 Ammonia

c Cycle

d Desorption

e Evaporator

en Environmental

h Heating

ps Sorbent

ref Refrigeration

s Sorption

Abbreviation

ENG Expanded natural graphite

ENG-TSA Expanded natural graphite treated by the sulfuric acid

GWP Global warming potential

M Metal elements

ODP Ozone depletion potential

X Cl

1. Introduction

Sorption refrigeration has great potential for the utilization of low grade energy, and that is essential for the energy conservation (Deng et al. 2011; Wang et al. 2012). Sorption refrigeration also has the feature of zero ODP (ozone depletion potential) and GWP (global warming potential) (Wang and Oliveira, 2006; Fan et al. 2007), which is important for the environmental protection.

Solid/gas sorption is divided into physical adsorption and solid chemisorption (Meunier, 1998). Compared with physical adsorption, solid chemisorption features the larger sorption quantity, which is attractive for increasing the specific cooling power per kilogram sorbent (SCP) and consequently decreasing the volume of the refrigerator. The equilibrium sorption processes of physical adsorption have two variables, such as p and T , whereas the equilibrium solid chemisorption process is monovariant. The Clapeyron diagrams are widely used for the analysis of the solid sorption performances (Neveu and Castaing, 1993). For example, Wang et al. (2004) suggest that composite sorbents can improve the mass transfer performance of chemical sorbents in vacuum system and can restrain the agglomeration phenomenon. Gong et al. (2012) proposed and manufactured a novel composite sorbent - methanol sorption chiller, and results show that it can improve SCP and COP. Yan et al. (2014) studied the ammonia sorption characteristics on composite sorbent of CaCl_2 and multi-walled carbon nanotubes. Wang et al. (2009) studied the performances of sorption refrigerating working pairs by equilibrium curves.

However the actual refrigeration processes are non-equilibrium processes (Aristov et al. 2008), it will inevitably lead to errors if the performances are analyzed under equilibrium conditions. On this aspect Wang et al. (2008) studied MnCl_2 and CaCl_2 and found that they have multi-step reaction processes with ammonia. Trudel et al. (1999) researched on $\text{CoCl}_2\text{-NH}_3$

working pair and suggested that the solid–gas equilibrium curves are more complex than theoretical single equilibrium line; therefore they put forward the theory of pseudo balance. That means both temperature and pressure need to be specified in order to determine the working performance. Namely the system is bivariant other than monovariant. Aidoun and Ternan (2001) further studied the pseudo steady state transformation and instability.

For analyzing the working processes of chemical sorbents Lebrun and Spinner (1990) established the basic chemisorption kinetic model. On this basis Mazet et al. (1991) proposed the overall reaction model, Goetz and Marty (1992) established the phenomenological model based on the concept of the grain-pellet. For physical adsorption processes Rand (1976) developed the model that is called the Dubinin-Polanyi potential model. After that Critoph (1988) developed the simplified D - A equation that is widely recognized.

But almost all the models mentioned above are for the equilibrium sorption conditions, and there are few researches on the non-equilibrium sorption kinetics. In order to investigate the influence of non-equilibrium conditions on the solid chemisorption refrigeration performances, $\text{MnCl}_2\text{-NH}_3$, $\text{CaCl}_2\text{-NH}_3$, and $\text{NH}_4\text{Cl-NH}_3$ working pairs are researched in this paper. The kinetic models are studied and the relation between the desorption hysteresis phenomena and reaction heat is analyzed by the Arrhenius equation.

2 Sorbents and test unit

2.1 Preparation of the Sorbents

The matrix of expanded natural graphite (ENG) and the ENG treated by the sulfuric acid (ENG-TSA) could improve the heat and mass transfer processes of sorbent greatly due to its high

thermal conductivity and reasonable gas permeability for preventing agglomeration phenomenon (Lu et al. 1996; Oliveira et al. 2007, Wang et al. 2011), thus ENG-TSA is used as the inert porous additive of the chlorides. The procedures for producing the sorbents are shown in reference written by Jiang et al. (2014). First the ENG-TSA is dried in the oven, and then ENG-TSA is mixed with a solution of chloride and is dried at 160°C. Some chlorides need higher temperature to remove crystal water. At last, the composite powder are compacted in the reactor as the consolidate blocks.

2.2 Experimental procedures and calculation of sorption quantity

The non-equilibrium sorption performance test unit is shown in Fig.1a. The test units have two sorption beds, one refrigerant vessel, three cryostats, a pressure transmitter and valves, etc. The vessel acts as condenser or evaporator, depending on the operation conditions. Temperature of sorption beds and the refrigerant vessel is controlled by three cryostat baths. Fig. 1b shows the photo of the test unit.

Fig.1. Test unit of sorption performance, (a) Scheme of testing unit; (b) Photo of testing unit;

2.2.1 The testing procedures of non-equilibrium curves

The procedures are as follows:

(1) First the temperature of refrigerant vessel (serves as condenser) is controlled by one cryostat at the condensing temperature. The sorbent is filled in the sorption bed 1, for which the temperature is controlled by one cryostat at the desorption temperature. In this process valves V1 and V3 are open, and valves V2 and V4 are close. The refrigerant sorbed by the sorbent in bed 1 desorbs to the condenser and condenses there, and the data is collected by the data collector. For a fixed condensing temperature the desorption process of sorbent completes when the level in the refrigerant vessel reaches a predetermined value.

(2) After the first step the valve V1 is closed. The temperature of the sorbent bed is controlled by the cryostat from the highest desorption temperature of about 150°C to the environmental temperature, and for each test point the temperature and pressure of the bed are collected when the data doesn't change for five minutes.

2.2.2 The testing procedures of isobaric sorption/ desorption curves

The procedures are as follows:

(1) Open the valves V1 and V3. Keep the refrigerant vessel at a constant pressure, control the temperature of sorbent bed 1 decreasing from high temperature to room temperature slowly. For each test point with predetermined refrigerant temperature and sorption temperature the fluid level in the refrigerant vessel is recorded when the data doesn't change at least for 5 minutes.

(2) In a similar manner the bed is heated in the desorption process, and the data of the refrigerant level in the refrigerant vessel is recorded.

2.2.3 Calculation of sorption quantity

The sorption quantity of sorbent is calculated by the refrigerant level in the refrigerant vessel, and the equation is:

$$x = \frac{1}{m} \cdot \left\{ \left[1 - \frac{v'(T_e)}{v''(T_e)} \right] \cdot \frac{A_e}{g} \cdot \Delta(\Delta p) + \frac{\Delta V}{v''(T_e)} \right\} \quad (1)$$

where x is sorption quantity (kg kg^{-1}), Δp is the pressure difference between the two ends of ammonia column, $\Delta(\Delta p)$ is the difference between the data in sorption/desorption process and the initial data (Pa), m is the sorbent mass (kg), A_e is the effective area of cross section of ammonia in the evaporator/ condenser (m^2), g is the gravity acceleration ($9.80 \text{ m} \cdot \text{s}^{-2}$), $v'(T_e)$ and $v''(T_e)$ are specific volume of saturated liquid ammonia and saturated vapor ammonia ($\text{m}^3 \text{ kg}^{-1}$), ΔV is the volume from the valve V_3 to the inside of the bed 1 (m^3), and it is only considered for the first adsorption process because it is vacuum. For the following experiments it can be neglected because the channel is filled by the ammonia vapor and the change of the specific volume of the ammonia vapor is very small and can be neglected.

The sorbent mass is measured by the balance (BS2202S) with a measuring error of 0.01 g. The pressure difference between the vapor end and liquid end of the evaporator/ condenser is tested by the smart pressure transmitter (Fig.1b), whose testing error is 0.2%. According to Eq. (2) and neglected the error caused by the last item in eq.(2), the maximum relative errors of sorption/ desorption quantities of sorbent is 3.66%.

$$|dx| = \left| - \left(1 - \frac{v'(T_e)}{v''(T_e)} \right) \cdot \frac{A_e \times dm}{m^2 \cdot g} \cdot \Delta(\Delta p) + \left(1 - \frac{v'(T_e)}{v''(T_e)} \right) \cdot \frac{A_e}{m \cdot g} \cdot d(\Delta(\Delta p)) \right| \quad (2)$$

$$\left| \frac{dx}{x} \right| \leq \left| \frac{dm}{m} \right| + \frac{d(\Delta(\Delta p))}{\Delta(\Delta p)}$$

4. Experimental results and discussions

4.1 The Clapeyron curves of metal chlorides under non-equilibrium conditions

The Clapeyron curves of $\text{MnCl}_2\text{-NH}_3$ under the non-equilibrium conditions is tested by the procedures as shown in 2.2.1, and the results are shown in Fig.2.

Fig.2 The experimental and theoretical lines of $\text{MnCl}_2\text{-NH}_3$ working pair

In Fig.2 the theoretical line is for the equilibrium theoretical Clapeyron line shown in reference written by Neveu and Castaing (1993), which is fitted by the equation:

$$\ln p_{\text{NH}_3} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (3)$$

Where p_{NH_3} is the ammonia pressure (Pa), R is gas constant ($\text{kJ mol}^{-1}\text{K}^{-1}$), T is the sorption temperature (K), ΔS is the reaction entropy ($\text{kJ mol}^{-1}\text{K}^{-1}$), ΔH is reaction enthalpy (kJ mol^{-1}).

The data of ΔS and ΔH are obtained from the reference written by Neveu and Castaing, 1993.

Fig.2 shows that the experimental non-equilibrium Clapeyron lines for the $\text{MnCl}_2\text{-2NH}_3$ are parallel to theoretical line, but much different from the theoretical one. The more ammonia sorbed the larger difference between the theoretical and experimental results. Such a result indicates the

experimental sorption/ desorption performance of MnCl_2 has binary variables of p and T other than single variable of p or T .

Like MnCl_2 the non-equilibrium curves of $\text{CaCl}_2\text{-NH}_3$ show the similar trends, which are in Fig. 3. The lines for $\text{CaCl}_2\text{-4NH}_3$, $\text{CaCl}_2\text{-5NH}_3$, and $\text{CaCl}_2\text{-6NH}_3$ are very close to the theoretical line, whereas the lines of $\text{CaCl}_2\text{-7NH}_3$ and $\text{CaCl}_2\text{-8NH}_3$ are far away from the theoretical equilibrium line. It implies the sorption process of $\text{CaCl}_2\text{-7NH}_3$ and $\text{CaCl}_2\text{-8NH}_3$ can only happen when the sorption temperature is much lower than the theoretical temperature.

Fig.3 The experimental and theoretical lines of $\text{CaCl}_2\text{-NH}_3$ working pair

It is difficult to get the experimental curves of NH_4Cl and NH_3 because its theoretical equilibrium Clapeyron line is close to that of NH_3 . Just like Fig.4 shows that the experimental line of $\text{NH}_4\text{Cl-3NH}_3$ is very close to that of NH_3 . It is mainly because of that the reaction heat of $\text{NH}_4\text{Cl-NH}_3$ working pair is only slightly larger than the vaporization enthalpy of NH_3 . The performance of $\text{NH}_4\text{Cl-NH}_3$ working pair is much different from the $\text{MnCl}_2\text{-NH}_3$ and $\text{CaCl}_2\text{-NH}_3$ working pairs. The lines of $\text{NH}_4\text{Cl-2NH}_3$ and $\text{NH}_4\text{Cl-NH}_3$ are slightly below theoretical equilibrium line. The reason is analyzed, and it is related with the porous structure of the

ENG-TSA, which has the capillary force for the NH_3 liquid and makes the sorption process happen when the temperature is high. The results also indicate that the sorption process of $\text{NH}_4\text{Cl}-\text{NH}_3$ has binary variables because it has several curves other than single theoretical curve in the experiments.

Fig.4 The experimental and theoretical lines of $\text{NH}_4\text{Cl}-\text{NH}_3$ working pair

The experimental sorption/ desorption Clapeyron curves of chlorides- NH_3 are bivarient. Such a result firstly means that the equilibrium lines cannot be used for simulating the sorption performance; otherwise there will be a big error. Secondly such a phenomenon will lead to the performance difference between the sorption and desorption. The isobaric sorption/ desorption performances are test in order to verify that.

4.2 The isobaric sorption/ desorption curves of chlorides-ammonia

The isobaric sorption/ desorption performances are tested as the procedures shown in 2.2.2.

The results of $\text{MnCl}_2-\text{NH}_3$ working pair under the pressure of 4.3 bar is shown in Fig.5. In Fig.5 the ‘Experimental results of Fig.2’ is obtained from the experimental Clapeyron curves in Fig.2 by taking the pressure of 4.3 bar. Fig.5 shows that the actual isobaric sorption curve of

$\text{MnCl}_2\text{-NH}_3$ working pair fits the experimental results of Fig.2 very well, but the isobaric desorption line is much different from the experimental results of Fig.2. It means if the experimental Clapeyron curves are used for simulating the refrigeration performance, the data will have a big error because the actual desorption process has the significant hysteresis phenomenon. Fig.5 shows that the largest hysteresis happens for the $\text{MnCl}_2\text{-4NH}_3$ when the corresponding heat source temperature is about 110°C . Such a data is lower than the equilibrium desorption temperature of 120°C . The hysteresis phenomenon is weaker when the ammonia in the ammoniate MnCl_2 is less. It almost disappears when the sorption quantity is nearly $2\text{mol NH}_3 \text{ mol}^{-1} \text{MnCl}_2$.

Fig.5 Isobaric sorption/ desorption curves of $\text{MnCl}_2\text{-NH}_3$ under the condition of 4.3 bar

Similar with the $\text{MnCl}_2\text{-NH}_3$ working pair, the $\text{CaCl}_2\text{-NH}_3$ has similar trends (Fig.6). The isobaric sorption curve in Fig.6 is close to the experimental results in Fig.3, but the desorption curve is much different. The significant hysteresis phenomenon happens for the $\text{CaCl}_2\text{-7NH}_3$. Comparing the results with the results in Fig.3, the serious desorption hysteresis happens when the experimental Clapeyron line is far from the theoretical equilibrium line, i.e. when the sorption quantity is larger.

The hysteresis happens for $\text{NH}_4\text{Cl-NH}_3$ working pair as well, and the results are shown in

Fig.7. For $\text{NH}_4\text{Cl-NH}_3$ both the isobaric sorption curve and isobaric desorption curve are close to the experimental results in Fig.4, and the hysteresis phenomena can almost be neglected.

Fig.6 Isobaric sorption/ desorption curves of $\text{CaCl}_2\text{-NH}_3$ under the condition of 4.3 bar

Fig.7 Isobaric sorption/ desorption curves of $\text{NH}_4\text{Cl-NH}_3$ under the condition of 4.3 bar

The results shown in Fig.5, 6 and 7 are compared, and the hysteresis is more serious when the sorbent requires higher desorption temperature. It is mainly related with the desorption heat that depends on the activated energy for the desorption process. For the desorption process the desorption activation energy is the sum of the activated energy for sorption process and the reaction heat, and in which the reaction heat is much larger than the activated energy for sorption process. Thus for $\text{MnCl}_2\text{-NH}_3$ working pair the desorption activated energy is highest, followed by

$\text{CaCl}_2\text{-NH}_3$ and then $\text{NH}_4\text{Cl-NH}_3$ working pair. Such a result coordinates with the hysteresis phenomena of different working pairs.

Further analyzing the mechanism of desorption hysteresis of $\text{MnCl}_2\text{-NH}_3$ in Fig.5, the serious desorption hysteresis occurred for $4\text{mol NH}_3 \text{ mol}^{-1} \text{MnCl}_2$. Such a phenomenon can be explained by the structure and crystal field theory of ammoniate MnCl_2 . The energy level of five orbits is different for ammoniate MnCl_2 by the action of the surrounding ligands degeneration. Such a level splitting phenomenon will bring the extra stabilization energy, i.e. crystal field stabilization energy, under the condition of d orbits not full. For $\text{MnCl}_2\text{-2NH}_3$ the ligands occupy sp orbit, for $\text{MnCl}_2\text{-4NH}_3$ ligands occupy sp_3 orbit, and for $\text{MnCl}_2\text{-6NH}_3$ the ligands start occupying d orbit (Wang et al., 2009). Thus the desorption process from $\text{MnCl}_2\text{-6NH}_3$ to $\text{MnCl}_2\text{-4NH}_3$ needs more energy, and correspondingly the serious hysteresis happens. Likewise, the desorption hysteresis is serious for the desorption process from $\text{CaCl}_2\text{-8NH}_3$ to $\text{CaCl}_2\text{-4NH}_3$, i.e. $7\text{mol NH}_3 \text{ mol}^{-1} \text{CaCl}_2$ in Fig.6.

4.3 The kinetic models of chlorides-ammonia working pairs

For the sorption/ desorption process with double variables, the characteristics of the working pair can be analyzed by the D-A equation amended by Critoph (Critoph, 1988). Such as the experimental Clapeyron curves of chlorides, they are bivariate, and the D-A equations are applicable. Likewise, the experimental isobaric sorption process close to the experimental Clapeyron curves, thus the D-A equation can be used for simulating the kinetic sorption process. For different working pairs, the D-A equation is:

$$x = x_0 \exp \left[-k \left(\frac{T}{T_{ref}} - 1 \right)^n \right] \quad (4)$$

Where x is sorption quantity (kg kg^{-1}), T_{ref} is refrigeration temperature, k and n are constants for the refrigerant.

The constants in Eq.4 are summarized in Table 1.

Table1 The coefficients of D-A equation for sorption working pairs

Working pairs	x_0	k	n
MnCl ₂ -NH ₃	0.6911	3.345	1.713
CaCl ₂ -NH ₃	1.2224	6.388	1.857
NH ₄ Cl-NH ₃	0.668	40.9	1.578

For the desorption process the hysteresis makes the deviation between the isobaric desorption curves far from the experimental Clapeyron curves. The relation between such a phenomena and the reaction heat is analyzed by the Arrhenius equation (Marcio and Jose, 2007), which is for the relation between the sorption rate and the temperature.

$$\ln K = \ln A - \frac{E}{RT} \quad (5)$$

where K is the constant, A is frequency factor, E is activation energy of the reactants (kJ mol^{-1}).

The complexation process between the chlorides and ammonia:

where M is metal elements; X is Cl; a , b , m , and n are reaction equilibrium coefficients.

Sorption velocity can be calculated by:

$$r_s = K_s M_a X_b (NH_3)_n^{c_1} (NH_3)^{c_2} \quad (7)$$

and K_s in the equation is:

$$\ln K_s = \ln A_s - \frac{E_s}{RT} \quad (8)$$

Desorption velocity is calculated by:

$$r_d = K_d M_a X_b (NH_3)_m^{c_3} \quad (9)$$

where K_d is:

$$\ln K_d = \ln A_d - \frac{E_d}{RT} \quad (10)$$

In the Eqs. 7-10, K_s and K_d are constants, E_s is sorption activation energy (kJ mol^{-1}), E_d is desorption activation energy (kJ mol^{-1}).

For equilibrium desorption condition, namely $r_s = r_d$:

$$K_s M_a X_b (NH_3)_n^{c_1} (NH_3)^{c_2} = K_d M_a X_b (NH_3)_m^{c_3} \quad (11)$$

$$K_d / K_s = M_a X_b (NH_3)_n^{c_1} (NH_3)^{c_2} / M_a X_b (NH_3)_m^{c_3} = K \quad (12)$$

The equilibrium constant is:

$$\begin{aligned} \ln K = \ln \frac{K_d}{K_s} &= \ln A_1 - \frac{E_d}{RT} - \ln A_2 + \frac{E_s}{RT} = \ln A_0 - \frac{\Delta H}{RT} \\ \ln K &= \ln x_{(\text{for desorption})} - \ln x_{(\text{for sorption})} \end{aligned} \quad (13)$$

Where A_0 is a constant, related with the type of metal chloride, x is sorption quantity (kg kg^{-1}).

So the relationship between desorption hysteresis and reaction heat is as follows:

$$\begin{aligned} \ln K &= \ln x_{(\text{for desorption})} - \ln \left\{ x_0 \exp \left[-k \left(\frac{T}{T_{ref}} - 1 \right)^n \right] \right\} = \ln A_0 - \frac{\Delta H}{RT} \\ \ln x_{(\text{for desorption})} &= \ln \left\{ x_0 \exp \left[-k \left(\frac{T}{T_{ref}} - 1 \right)^n \right] \right\} + \ln A_0 - \frac{\Delta H}{RT} \end{aligned} \quad (14)$$

Because the reaction heat of $\text{MnCl}_2\text{-NH}_3$ and $\text{CaCl}_2\text{-NH}_3$ are larger, the desorption hysteresis is serious. The reaction heat of $\text{NH}_4\text{Cl-NH}_3$ working pairs is smaller, and the hysteresis can be

neglected (both sorption and desorption curves are closed to the experimental Clapeyron curves).

Thus only the desorption hysteresis of $\text{MnCl}_2\text{-NH}_3$ and $\text{CaCl}_2\text{-NH}_3$ are analyzed. By Eq. 14, for Manganese chloride A_0 is 18.02, and for Calcium chloride A_0 is 17.37. The comparison of the fitting results by Eq.14 and the experimental results are shown in Fig.8 and Fig.9. Results show that when the reaction heat is bigger, the simulation error is smaller. Such as $\text{MnCl}_2\text{-NH}_3$, its reaction heat is $47.416 \text{ kJ}\cdot\text{mol}^{-1}$ and the biggest error between the simulation and the experiments is 3.1%. For the $\text{CaCl}_2\text{-NH}_3$ the reaction heat is $41.013 \text{ kJ}\cdot\text{mol}^{-1}$, correspondingly the biggest error of 9.8%.

Fig.8 Comparison between the experiments and Arrhenius equation for $\text{MnCl}_2\text{-NH}_3$ working pair

Fig.9 Comparison between the experiments and Arrhenius equation for $\text{CaCl}_2\text{-NH}_3$ working pair

4.4 The analysis on the intermittent refrigeration cycle

Under the condition of heating process from 70°C to 180°C, 25°C cooling temperature, and 0°C refrigeration temperature, the intermittent refrigeration cycle with the MnCl_2 is analyzed by theoretical equilibrium lines, experimental results, and fitted equations. COP is calculated.

$$COP = \frac{Q_{ref}}{Q_h} = \frac{m \times \Delta x \times L_a - m \times \Delta x \times c_{am}(T_{en} - T_e)}{m \times \Delta x \times \Delta H + \int_{T_{en}}^{T_h} (mc_{ps} + m \times x \times c_{am}) dT} \quad (15)$$

where Q_{ref} is refrigerating capacity (kJ), Q_h is heating capacity (kJ), Δx is the cycle sorption quantity of sorbent (kg kg^{-1}), L_a is latent heat of ammonia (kJ kg^{-1}). c_{am} is the specific heat capacity of ammonia ($\text{kJ kg}^{-1}\text{K}^{-1}$), T_{en} is the environmental temperature, T_e is the evaporation temperature (K), c_{ps} is the specific heat of sorbent ($\text{kJ kg}^{-1}\text{K}^{-1}$), T_h is the highest heating temperature (K).

$$SCP = \frac{Q_{ref}}{t_c \times m} \quad (18)$$

where t_c is the cycle time (s), which is taken as 1800s.

Analysis shows that the theoretical COP is 0 if heating temperature is below 130°C. If heating source is higher than 130°C the theoretical COP is about 0.37 (shown in Fig.10a). However, experimental line shows that COP slowly changes as temperature increases, and its value changes from 0.287 to 0.352. The error bars are added for the experimental line, and the error caused by the testing processes mostly within 5%. The COP is also calculated by the D-A equation and the relationship between desorption hysteresis and reaction heat mention above, and the results (Fig.10a) show that fitting line agrees with the experimental line well, and most data fall within the ranges inside the error bars of experimental data. The maximum deviation is around 6.8%. But if the results analyzed by theoretical equilibrium lines the maximum error can reach

32%. Similarly the theoretical SCP is for the heating source temperature higher than 130°C is 268.48 W kg⁻¹. And experimental line show that its value changes from 126.41 to 195.21 W kg⁻¹. Fig.10b shows that fitting line by the D-A equation and Arrhenius equation coincides with the experimental line, and almost all the data fall within the ranges inside the error bars. The data calculated by the theoretical equilibrium line has a big error, and the maximum error is over 100%, which is around 107%.

The results in Fig. 10 indicate that the theoretical equilibrium line, which is extensively used for analyzing the refrigerating performance, is not applicable for the real non-equilibrium refrigerating conditions because its error is larger than 30%. The non-equilibrium lines and the relationship between desorption hysteresis and desorption enthalpy should be considered for simulating the sorption refrigeration performance of chlorides-ammonia working pairs.

Fig.10 Comparison among the experimental results, fitting line by D-A equation and Arrhenius equation for MnCl₂ -NH₃. (a) COP; (b) SCP

6 Conclusions

Three metal chlorides-ammonia working pairs are investigated. The experimental results

indicate that the features of non-equilibrium sorption/ desorption is different from the equilibrium performances.

(1) The experimental results show that the experimental Clapeyron curves of different chloride-ammonia working pairs are bivariant other than monovariant. They are influenced both by the temperature and pressure.

(2) The isobaric sorption/desorption performances are tested, and there is serious desorption hysteresis for $\text{MnCl}_2\text{-NH}_3$ and $\text{CaCl}_2\text{-NH}_3$ working pairs. The isobaric sorption curves for different chlorides and desorption curve of $\text{NH}_4\text{Cl-NH}_3$ are close to the experimental Clapeyron curves. For MnCl_2 and CaCl_2 the largest difference is less than 10%, and for NH_4Cl_2 the largest difference is around 20~30%. The desorption curves of $\text{MnCl}_2\text{-NH}_3$ and $\text{CaCl}_2\text{-NH}_3$ working pairs are far from the experimental Clapeyron curves because of the hysteresis, and the difference is as high as 60~70%.

(3) The bivariant processes for sorption are modeled by the D-A equation, and the hysteresis desorption processes are modeled by the Arrhenius equation. The intermittent refrigeration cycle of $\text{MnCl}_2\text{-NH}_3$ is analyzed under the condition of heating source temperature from 70°C to 180 °C, 25 °C cooling source, and 0°C refrigeration temperature. Compared with the experimental results most data of fitting curves fall within the range surrounded by error bars of experimental data, while the error of equilibrium theoretical Clapeyron curves is as high as 107%. Such a result indicates that for simulating the refrigeration performance the non-equilibrium performance needs to be considered other than the theoretical equilibrium performance, which will lead to big error.

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