Method for determining effect of kinetics and heat-transfer on the adsorption rate of ammonia on LiCl

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Abstract

From literature, it is known that cycle-times of chemical heat pumps can be limited by kinetic behavior of the sorbens and by the heat transfer of the system. Because increased cycle times result in reduced power density of a heat pump system, it is vital for developing (commercially viable) chemical heat pump systems to determine the rate-limiting factor.

This paper presents a method for determining the rate-limiting factor by measuring the gas pressure and temperature over a LiCl-sample as a function of the amount of ammonia. The results are compared with two models: one model that assumes fast kinetics and thereby making the transfer of heat from the salt to the surroundings the rate-limiting factor, whereas the second model assumes fast heat transfer and adsorption kinetics to be the rate-limiting factor.

Results show a very good correlation between the measurements and the heat transfer model whereas the correlation between the measurements and the adsorption kinetics model is considerably less. Therefore, it is concluded that adsorption of LiCl for the system presented here is limited by heat transfer.

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1.   Introduction

Chemical heat pumps and heat transformers have been studied at the Energy research Centre of the Netherlands (ECN) because they operate without using electric power and can contribute to energy efficiency in the industry by using waste heat to drive them that would otherwise be (actively) released to the environment.

One of the systems currently developed, is a chemical heat transformer based on ammonia adsorption and desorption onto salts. Aiming at a heat transformer for temperature lifts of over 60ºC in the range of 80ºC to 150ºC waste heat, LiCl and $MgCl_2$ were chosen as respectively the low and high temperature salts, based on the following sorption reactions with ammonia:

$LiCl^.1NH_3$ + 2 NH_3 ↔ $LiCl^.3NH_3$ + heat
$MgCl_2^.2NH_3$ + 4 NH_3 ↔ $MgCl_2^.6NH_3$ + heat
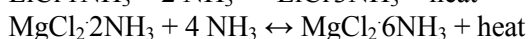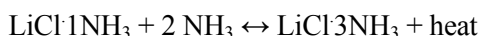
Considering the poor thermal conductivity of these salts (approximately 0.1 $Wm^{-1}K^{-1}$ [[1]]) and the tendency of salts to degrade and leave their matrix, a method was developed to deposit these salts into metal foam, which would increase the thermal conductivity and reduce the mobility of the salts.

Therefore, the final design of the heat pump reactors incorporates this method by using a fin-tube type heat exchanger where each fin is coated with a layer of metal foam containing the ammonia salt. Figure 1.1 shows the design of the reactor with on the left hand side a cross-section of the reactor while the figure on the right shows the top view of the pipe-fin configuration.
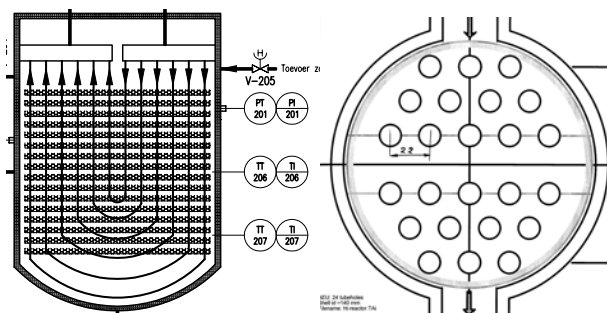

Figure 1.1 *Cross-section (left) and top-view (right) of reactor*

Each reactor contains about 1 kg of salt and generates approximately 2500 kJ of heat upon adsorption of ammonia. The power output is, however, depending on the rate at which this heat can be transferred to and from the reactors. Model calculations show typical cycle times of 1 hour, with 30 minutes of adsorption and 30 minutes of desorption. These calculations include thermal transfer limitations based on thermal conductivity and thermal transfer coefficients of the used materials but do not take into account the kinetics of the sorption reactions.

The relevance and impact of this parameter was shown by Aidoun [[2]] who showed for the adsorption of ammonia onto $CoCl_2$, not the transfer of heat was the limiting factor for the cycling times but the reaction rate for ammonia adsorption was. This raised the question whether the assumption of the model calculations that the cycling times of the heat transformer system were limited by heat transfer only was valid. Unfortunately, no reliable information was found on the kinetics of $MgCl_2$ or LiCl. Considering the relative high temperatures of the $MgCl_2$, kinetic limitations were considered unlikely for this salt. For LiCl, however, the temperatures are considerably lower and therefore kinetic limitations are more likely to occur.

In this paper, we present a simple method to determine the dominant factor in the process and show the results of this method when applied to measurements of the adsorption of ammonia to lithium chloride.

2.   Materials and methods

4 grams of LiCl is prepared and precipitated in a metal foam matrix, comparable with the matrix used in the sorption heat pump. The sample is subsequently placed inside a closed container with a volume of 200 ml as is schematically shown in Figure 2.1. The pressure and temperature of the gas inside this container is monitored using a PTX1400 pressure sensor with a range of 0-6 bar and a k-type thermocouple respectively. A trace-heater is used to keep the container at a temperature of $50^{o}C$.
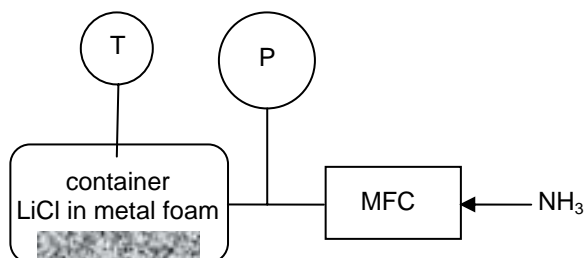

Figure 2.1 *Schematic overview of experimental setup*

At the start of the measurement, the container is evacuated. After the pressure has been at less than 5 mbar for at least 5 minutes, the valve to the vacuum pump is closed and a constant flow of ammonia is supplied using a Bronkhorst type F-201D mass flow controller with a range of 0-2 l_n/min NH_3. Together with the flow of ammonia, the measurement of the pressure and temperature is started. The measurement is stopped when a pressure of at least 4 bar has been reached.

The measurement has been conducted for mass flows of 50, 100, 150, 200 and 250 ml_n per minute. The flows were chosen such that the adsorption time was comparable with expected heat pump cycling times.

3. Model calculations

Two models have been used to describe the measurements. The *thermal transfer model* assumes adsorption is limited by heat transfer from the salt to the matrix and container. The *adsorption kinetics model* assumes the adsorption rate is limited by kinetics of the adsorption reaction.

The amount of ammonia adsorbed as a function of time is calculated from the amount of ammonia supplied and the amount of ammonia in the gas phase. From the mass flow rate the amount of ammonia as a function of time is calculated using:

$$m_{\text{total}}(t) = v \cdot t \,,$$

$m_{\text{total}}(t)$ total amount of ammonia in container at time *t;*
v mass flow (in g/s);
t time (s).

The amount of ammonia in the gas phase at time *t* is given by:

$$m_{\text{gas}}(t) = \frac{P(t)V}{RT(t)} \,,$$

$m_{\text{gas}}(t)$ amount of ammonia in the gas phase at time *t*;
$P(t)$ pressure at time *t;*
V volume of container;
R gas constant;
$T(t)$ temperature in container at time *t.*

The amount of ammonia adsorbed by LiCl at time *t* is then given by:

$$m_{\text{ads}}(t) = m_{\text{total}}(t) - m_{\text{gas}}(t)$$

$m_{\text{ads}}(t)$ amount of ammonia adsorbed at time *t*.

The amount of heat generated by adsorption of ammonia is given by:

$$Q_{\text{ads}}(t) = m_{\text{ads}}(t) \cdot \Delta H \,,$$

ΔH adsorption enthalpy ($J \cdot g^{-1}$);
$Q_{\text{ads}}(t)$ amount of adsorption heat at time *t* (J).

The amount of generated power is given by:

$$W_{\text{ads}}(t) = \frac{\partial Q_{\text{ads}}(t)}{\partial t}$$

$W_{\text{ads}}(t)$ power generated by adsorption at time *t* (W).

3.1 Thermal transfer model

This model assumes the kinetics of the adsorption reaction is rapid in comparison with the transfer of heat from the sorbens to the container. Hence, the pressure in the container equals the equilibrium pressure for $LiCl \cdot 3NH_3$. Based on this assumption, the adsorption temperature of the sorbens can be calculated from the measured pressure.

$$T_{ads}(t) = \frac{\Delta H}{\Delta S - R \ln(P(t))},$$

$T_{ads}(t)$ adsorption temperature at time t (K);
ΔS adsorption entropy ($J \cdot g^{-1} K^{-1}$).

The driving force for the heat transfer is then given by the difference in sorbens temperature and container temperature. The flux of heat from the sample to the container is then given by:

$$J(t) = U \cdot A \cdot (T_{ads}(t) - T_{con}(t)),$$

$J(t)$ heat flux from sample to container at time t (W);
U effective thermal transfer coefficient ($Wm^{-2}K^{-1}$);
A effective heat exchanging surface (m^2);
$T_{con}(t)$ temperature of container at time t (K).

For a steady state, the flux equals the generated power. For a non steady state, the flux is corrected for transfer of heat to and from the metal foam:

$$J(t) = W_{ads}(t) - C_{p,foam} \cdot m_{foam} \frac{\partial T_{ads}}{\partial t},$$

$C_{p,foam}$ heat capacity of foam ($Jg^{-1}K^{-1}$);
m_{foam} mass of foam (g).

From the above equations, only the parameters U and A are unknown and the product of the two can be calculated from the measurements. If the hypothesis of quick adsorption rates compared to thermal conductivity is correct, the $U \cdot A$ value should be independent of the mass flow rate.

3.2 Adsorption kinetics model

This model assumes heat transfer is quick compared to the kinetics of the adsorption reaction. The general equation for a reaction is given by:

$$\frac{\partial m_{ads}(t)}{\partial t} = a\mu,$$

a phenomenological constant
μ chemical activity.

The chemical activity of an isothermal reaction is expected to be proportional to the pressure difference between the equilibrium pressure and the actual pressure. For adsorption reactions, a dependence on amount of sorption sites can be expected. The latter effect can occur in many forms, depending on the type of sorption (e.g. BET, Langmuir). This relation is represented as $f(m_{ads})$:

$$\frac{\partial m_{ads}}{\partial t} = a \cdot \left(P(t) - P_{eq}(T) \right) \cdot f(m_{ads})$$

P_{eq} equilibrium pressure at temperature T;
$f(m_{ads})$ function dependent amount of adsorbed NH_3.

With the pressures and adsorption rate known, this leaves a and $f(m_{ads})$ as the unknown parameters. Similar to the *thermal transfer model*, $a \cdot f(m_{ads})$ is expected to be independent of the mass flow rate.

Both models provide a (combined) constant that is expected independent of mass flow rate. By determining the correlation between mass flow rate and the parameter, the models can be validated.

4.   Results

Figure 4.1 shows the amount of ammonia in the gas phase, adsorbed and in total as a function of time. Most of the ammonia is adsorbed to the LiCl at a pressure of just less than 1 bar.
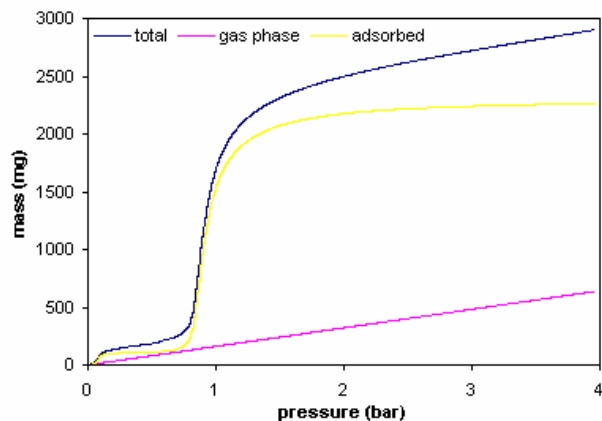
Figure 4.1 *Amount of ammonia as a function of time for a mass flow rate of 50 ml_n/min*

Figure 4.2 shows the value for the constant UA of the thermal transfer model as a function of the amount of ammonia adsorbed on LiCl calculated from the measured mass flow, temperature and equilibrium pressure. The UA value is very similar for mass flow rates from 100 to 250 ml_n per minute. The curve for the measurement at 50 ml_n per minute is somewhat lower in comparison.
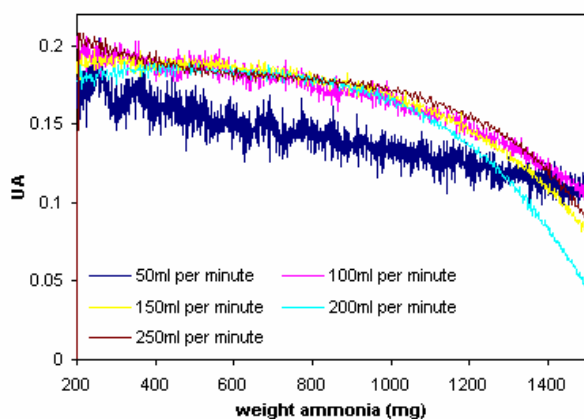
Figure 4.2 *UA as a function of amount NH_3 adsorbed*

Figure 4.3 shows the value for $a \cdot f(m_{ads})$ of the adsorption kinetics model as a function of the amount of ammonia adsorbed on LiCl calculated from the measured pressure and mass flow rate. The $a \cdot f(m_{ads})$ value decreases about 50% with increasing amount of ammonia adsorbed. There can also be a dependency of the mass flow rate observed: the value decreases with increasing mass flow rate. Similar to the previous graph, the measurement at a flow rate of 50 ml_n per minute deviates from the general trend.
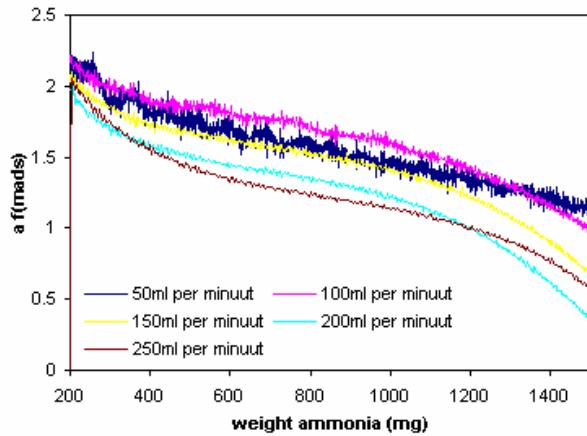
Figure 4.3 *a̓f(m*ads*) as a function of amount NH₃ adsorbed*

Considering the divergent behavior of the 50 ml$_n$ per minute measurement, this measurement is considered an outlier and is not used in the remaining calculations. A possible reason for this mass flow rate to result in an outlier is that this mass flow rate is quite small compared to the full scale of the mass flow controller. As the uncertainties of the mass flow controller scale with the full scale, this might have led to a relatively large deviation of the actual mass flow from the set value, which could explain the observed behavior.

Figure 4.4 and Figure 4.5 show the relative deviation from the average value of $U\!A$ and $a̓f(m_{ads})$ for each mass flow rate. These figures clearly show a strong dependency of the flow rate for the *adsorption kinetics model* where an increased flow results in a lower value for $a̓f(m_{ads})$. The *thermal transfer model* only shows some deviation from the average at the start and the end of the adsorption, and even that is without a clear flow dependency.
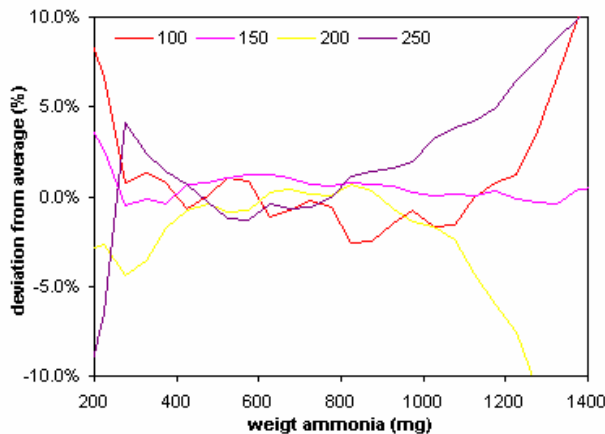

Figure 4.4 *Relative deviation from average value for $U\!A$ for each mass flow rate*
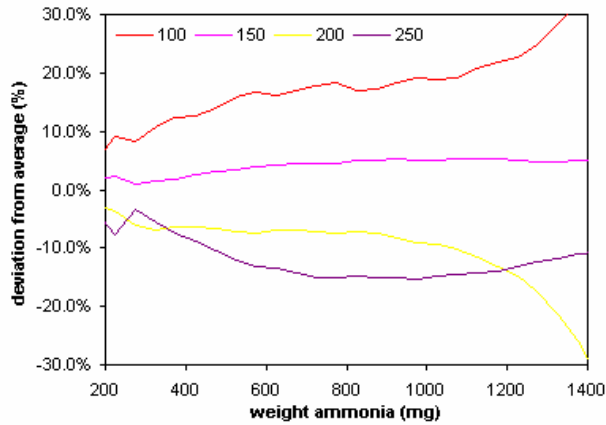
Figure 4.5 *Relative deviation from average value for a f(m_{ads}) for each mass flow rate*

From average value of UA and the size of the sample, the effective thermal conductivity of the sample has been estimated at 0.7 $Wm^{-1}K^{-1}$. For pure aluminum foam, this value would be too low as values ranging from 5 up to 10 $Wm^{-1}K^{-1}$ for this particular type of aluminum foam have been reported [[3]]. However, considering the generated heat has not only to transfer through the aluminum foam but also has to transfer through the salt, from the salt to the foam and from the foam through the sample holder to the bottom of the container, the estimated value of 0.7 $Wm^{-1}K^{-1}$ is not unrealistic.

5. Discussion and conclusions

The *thermal transfer model* shows good results for describing the adsorption of ammonia on LiCl·1NH$_3$ as no significant correlation between the model parameter $U\cdot A$ and the mass flow rate has been found. The *adsorption kinetics model* gives a poorer agreement. Furthermore it shows a decrease in $a\cdot f(m_{ads})$ with increasing flow rates. In case of combined heat transfer and kinetic limitations, it would be expected that kinetics increase with increased sample temperatures, thereby resulting in an increased value for $a\cdot f(m_{ads})$ with increasing mass flow rates rather than smaller values. Therefore, it is concluded that the *thermal transfer model* describes the process correctly and thus the adsorption of ammonia by LiCl is for the given conditions limited by transfer of heat from the sample.

Measurements at different temperatures could further support these conclusions. Increased thermal conductivity in combination with smaller adsorption times, which can be achieved by using smaller samples or increased mass flows, would allow determining the kinetic limitations for adsorption of ammonia onto LiCl.

For the development of our sorption heat pump based on ammonia sorption by LiCl/MgCl$_2$ these results mean that the used assumption in the model concerning the limiting processes and thus the calculated cycling times is correct. It also implies that cycling times can be further reduced by improving the thermal conductivity. Reduced cycling times means more sorption cycles can be executed in a given period of time, thereby increasing the total power output thus increasing the power density of the system and reducing the (capital) costs per unit of produced heat (or cold).

Using the method described in this paper on samples with enhanced thermal transport properties can reveal how much improvement could be made before kinetics becomes the limiting factor for the cycling times and thus the heat pumps performance.

Nomenclature

A	effective heat exchanging surface (m^2)
a	phenomenological constant
$C_{p,foam}$	heat capacity of foam ($Jg^{-1}K^{-1}$)
ΔH	adsorption enthalpy (Jg^{-1})
ΔS	adsorption entropy ($Jg^{-1}K^{-1}$)
$f(m_{ads})$	function dependent amount of adsorbed NH_3
$J(t)$	heat flux from sample to container at time t (W)
μ	chemical activity
$m_{ads}(t)$	amount of ammonia adsorbed at time t
$m_{total}(t)$	total amount of ammonia in container at time t
m_{foam}	mass of foam (g)
$m_{gas}(t)$	amount of ammonia in the gas phase at time t
v	mass flow (in g/s)
$P(t)$	pressure at time t
R	gas constant
$T(t)$	temperature in container at time t
$P(t)$	pressure at time t
P_{eq}	equilibrium pressure at temperature T
$Q_{ads}(t)$	amount of adsorption heat at time t (J)
$T_{ads}(t)$	adsorption temperature at time t (K)
$T_{con}(t)$	temperature of container at time t (K)
t	time (s)
U	effective thermal transfer coefficient ($Wm^{-2}K^{-1}$)
V	volume of container
$W_{ads}(t)$	power generated by adsorption at time t (W)

References

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3. V. V. Calmidi, R. L. Mahajan, The Effective Thermal Conductivity of High Porosity Fibrous Metal Foams, *J. Heat Transfer* 121, 466-471 (1999).