MISSION INNOVATION. IC7: AFFORDABLE HEATING AND COOLING OF BUILDINGS

SORPTION HEAT PUMP SYSTEMS (EP/V011316/1)

D1. Report on equilibrium and dynamic data for salts (and salt mixtures) for heat pumping, refrigeration and storage applications.

D1.1. Introduction and Theory

The purpose of this report is to summarise salt dynamic and equilibrium data for candidate salts (and salt mixtures), that use ammonia as refrigerant, for heat pump, refrigeration and storage applications.

Using ammonia with salt sorption reactions (adsorption and desorption) for heat pumping has the potential for increased Coefficient Of Performance (COP, akin to efficiency) systems, with scope for between 40 % and 60 % reductions in gas usage compared with existing (UK) condensing boilers.

The reported data references the enthalpy of transformation, ΔH [J/(mol)], and the entropy of transformation, ΔS [J/(mol·K)], for the ammonia salt reactions — values that relate to the Clausius-Clapeyron relationship for the phase transition of ammonia with the salt, (1).

$$\ln(p) = -\frac{\Delta H}{R_0 T} + \frac{\Delta S}{R_0} \tag{1}$$

The reaction coefficients reported refer to the number of moles of ammonia adsorbed onto the salt during a reaction, for reference the chemical reaction equation for a calcium chloride reaction with ammonia is shown in (2).

$$CaCl_2 \cdot 4NH_3 + 4NH_3 \rightleftarrows CaCl_2 \cdot 8NH_3 + Q_{4-8} \tag{2}$$

Q_{4-8} refers to the endothermic desorption heat or the exothermic adsorption heat, depending on the direction of the reaction. In this reaction, the reaction coefficients would be 4 and 8 (8 – 4 / 4 – 8).

D1.2. Testing Methods

To determine the data for the candidate salts, a number of different testing methods have been employed:

1. Large Temperature Jump (LTJ) method [1], applies conditions similar to that expected in a real machine, through imposing quick changes of temperature that initiate the sorption reactions. Pressure changes in the system are measured which allow analysis of the cycle to be conducted.
2. Isosteric Temperature Change (ITC) method, is similar in design to the LTJ method, measuring temperature and pressure, but there is no expansion volume and the heating/cooling takes place over several hours, rather than rapid heating over minutes in the LTJ. The purpose of the test is to track the equilibrium line to obtain accurate equilibrium data.

D1.3. Results

Table 1 summarises the equilibrium and dynamic data for a series of salts tested for heat pump and thermal transformation applications. With the exception of the SL salts (see note after table), the reported information is dynamic data of the salts as the reactions tested exhibit hysteresis between the adsorption and desorption reaction (different reaction temperature at the same pressure).

Table 1. Salt dynamic data from LTJ testing

Salt	Formula	Reaction[a]	Coefficients	*ΔH* / [J/(mol)]	*ΔS* / [J/(mol·K)]
Ammonium Chloride	NH_4Cl	SL	3 – 0 / 0 – 3	29 835	207
Sodium Bromide	NaBr	SL	5.25 – 0 / 0 – 5.25	30 159	207
Barium Chloride	$BaCl_2$	A	0 – 8	37 360	229
		D	8 – 0	48 925	264
Calcium Chloride	$CaCl_2$	A	4 – 8	32 845	208
		D	8 – 4	36 366	217
		A	4 – 2	31 700	202
		D	4 – 2	41 202	224
Manganese Chloride	$MnCl_2$	A	2 – 6	36 611	203
		D	6 – 2	58 196	254

[a] SL = Single Line, A = Adsorption reaction data and D = Desorption reaction data

ITC testing was used to investigate the salts that exhibit hysteresis and that show differences in the enthalpy of transformation (heat of reaction) between the adsorption and desorption reaction. ITC testing was proved to be successful as reactions lines formed within the previously measured LTJ lines, Figure 1, with the single heat of reaction data summarised in Table 2.

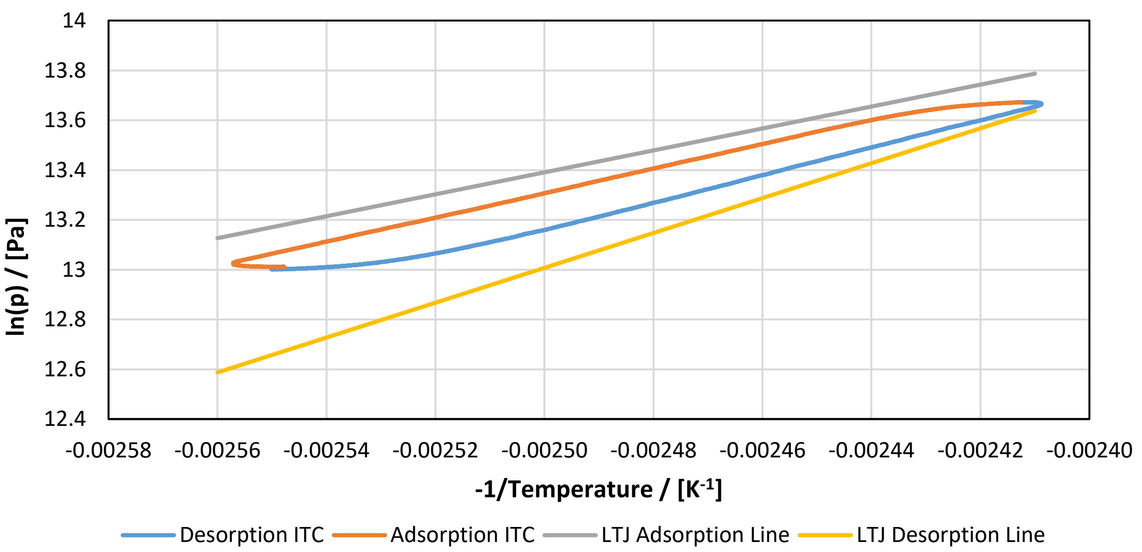

Figure 1. ln(p) vs. -1/T graph, illustrating the nature of an ITC output, with the ITC reaction lines falling within the previously obtained dynamic lines from LTJ testing ($MnCl_2$ test). An average of the ITC lines is used to obtain a single heat of reaction.

Table 2. Salt equilibrium data from ITC testing to obtain a single heat of reaction.

Salt	Formula	Coefficients	*ΔH* / [J/(mol)]
Barium Chloride	$BaCl_2$	8 – 0 / 0 – 8	40 745
Calcium Chloride	$CaCl_2$	8 – 4 / 4 – 8	42 080
		4 – 2 / 2 – 4	39 949
Manganese Chloride	$MnCl_2$	6 – 2 / 2 – 6	43 429

[1] Y. I. Aristov, B. Dawoud, I. S. Glaznev, and A. Elyas, "A new methodology of studying the dynamics of water sorption/desorption under real operating conditions of adsorption heat pumps: Experiment," *International Journal of Heat and Mass Transfer,* vol. 51, no. 19-20, pp. 4966-4972, 2008, doi: 10.1016/j.ijheatmasstransfer.2007.10.042.