Energy

Review

Deammoniation and ammoniation processes with ammonia complexes

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Abstract: For selecting the most suitable ammoniate as a heat storage material we have reviewed all the available literature since 1860. This data reveal that we can order the dissociation temperature and the enthalpy of reaction of different ammoniates. We show that all data can be represented by a single master curve. This curve shows that ammoniates belonging to the alkali metal periodic group have the lowest energy pro ammonia molecule, whereas transition metals (3d) have the highest energy pro ammonia molecule. These trends can be used to select the most suitable ammoniates under certain working conditions.

Keywords: ammoniate; heat storage; TCM; enthalphy; renewable energy

1. Introduction

A publication of Goldstein [1] marks the beginning of the renewed interest in salt hydrates, i.e. salts that contain a definite number of water molecules in the crystal lattice. Besides water, salts can also include solvents like ammonia, i.e., the so called ammoniates, and methanol, i.e., methanol solvates. The general equation for gas-solid equilibrium reactions will look like [2]:

$$\text{MX} \cdot n\text{L(s)} \rightleftharpoons \text{MX} \cdot m\text{L(s)} + (n - m)\text{L(g)}. \tag{1}$$

where MX·nL(s) is a solid salt complex formed from a salt MX·(m)L(s) and ($n - m$) mol solvent, which is present as vapor. The amount of L inside product MX is called the loading of the salt. The decomposition reaction of MX·nL is endothermic, i.e. it consumes energy ($-\Delta_r H_{m \to n}$), whereas in the exothermic formation reaction of MX·nL energy ($\Delta_r H_{m \to n}$) is produced. Hence, this system is ideal for storing heat loss-free: an ideal "heat battery". The operational parameters for this equilibrium reaction

are the vapor pressure of solvate L and the stored chemical energy inside the salt complex. By applying a high vapor pressure complexes with a higher loading of solvate will be formed and heat is generated. In contrast, upon applying energy to the salt complex by increasing the temperature, the salt complex will decompose.

Table 1. The main characteristics of three solvents for heat storage in solvent complexes [3, 4, 5].

Solvent	NH_3	CH_3OH	H_2O
Vapor pressure at 300 K (MPa)	1.2	0.05	0.012
Boiling temperature (K)	240	337	373
Melting temperature (K)	196	176	273.2
Flammability (%)	15-25	6-36	-
Toxicity (ppm) (US PEL)	50	200	-

The possibility to control the heat release and storage just by two parameters, i.e., temperature and vapor pressure, makes gas-solid reactions a promising system for heat storage applications. For a particular heat storage system in the build environment, the solvent should be selected based on the vapor pressure at the desired working conditions. This vapor pressure is preferably around 0.1–10 MPa at the temperature range where the system is operational. A high vapor pressure increases the rate of reaction of the solvent with the ammoniates [6], but in general at high vapor pressures additional safety precautions are needed. Three main solvents [2, 7] can be identified as options for heat storage by thermochemical reactions: water, ammonia and methanol. Each solvent has a specific set of working conditions, as decomposition temperature and solvent pressure, in combination with a certain type of salt. Also the toxicity and explosive limits have to be taken into account in choosing a salt and a solvent for a certain application. In Table 1 the main characteristics of the pure solvents are given. It shows that by increasing the working pressure respectively ammonia, methanol and water have to be selected.

Advantages of heat storage based on a solid-gas reaction (Thermochemical materials TCM's) are the relatively high energy density of 0.5–2 GJ/m^3, storage without loss of heat and relatively low costs of storage materials [8]. The current application of the TCM is foreseen on heat storage for domestic environment. By using materials like ammonia and methanol, heat storage is probably decentralized stored at district level, as the safety regulation with ammonia and methanol are strict. In case the reaction is with water, the heat storage system can be stored in houses. The high energy density and no loss of heat during storage period make this system favorable above a more simplified system like sensible heat storage.

In general, salts in combination with water are well described and information about crystal structures, thermochemical characteristics and densities can be found in extensive compilations of chemical data like the Gmelin ([9]). In contrast, salt complexes in combination with methanol and ammonia are rarely mentioned in literature. Indeed, about methanol complexes literature is hardly available [7]. Ammonia salt complexes have been well studied in the past.

In this paper our goal is to summarize this large set of thermodynamic data of salt complexes with ammonia to be able to identify the most suitable ammoniates for a heat storage system in domestic environment. In the first section, we will give a flavor of the large history in ammonia research and an overview of the ammoniates. The next section we will summarize the observations and these will be

discussed afterwards.

2. Ammoniates

In the second half of the 19th century, the first articles were published about the dissociation pressures of ammoniates at constant temperature. The first articles published dealt with chloride complexes [10, 11]. After the development of the heat theorem of Nernst [12], as first published in 1906, more research was performed on ammoniates. In this research the focus was mainly on the decomposition schemes of the ammoniates by varying the ammonia partial pressure at constant temperature [13, 14, 15, 16].
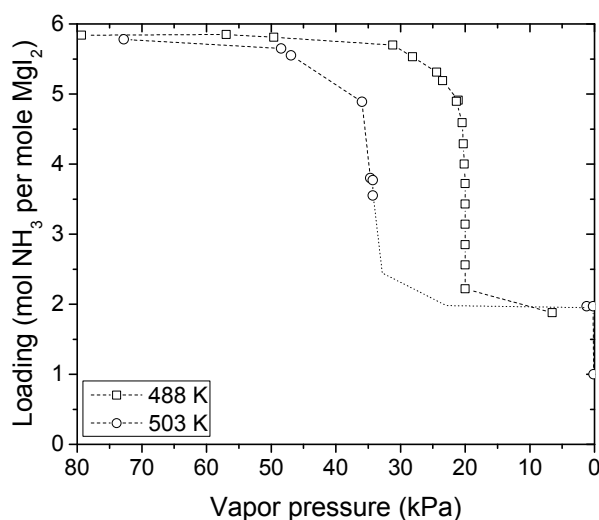

Figure 1. The dissociation pressure curve of MgI$_2$·6NH$_3$ at two different temperatures (488 and 503K, respectively) [17].

The most detailed investigations were done by two research groups in the beginning of the 20th century. These two groups studied a large number of salt complexes, using similar procedures as mentioned above. Firstly, they grew highly loaded ammoniates, which were decomposed by changing the ammonia pressure at constant temperature. Examples of the isotherms are given in Figure 1, showing the decomposition of MgI$_2$·6NH$_3$ at two temperatures, i.e. 488 K and 503 K. As can be seen, in case the system is equilibrated at a higher temperature, the decomposition starts at a higher vapor pressure. After recording these curves, $\Delta_r H^0$ was calculated. This is called the enthalpy of reaction, which is defined by the energy necessary to decompose an ammoniakate into a lower ammoniated salt and ammonia (MX·nNH$_3$(s) + $\Delta_r H^0_{m \to n} \rightleftharpoons$ MX·mNH$_3$(s)(s) + ($n - m$)NH$_3$(g)). The basic thermodynamic equation for the equilibrium between a condensed phase (solid or liquid) and the vapor phase of a pure substance, under conditions of low pressure, is used for this [18]:

$$\ln \frac{p}{p^0} = \frac{\Delta H^0_{m \to n}}{RT} - \frac{\Delta S^0_{m \to n}}{R}, \tag{2}$$

where p is the decomposition vapor pressure in Pa, p^0 is the reference vapor pressure of 10^5 Pa, $\Delta_r H^0_{m \to n}$ is the standard enthalpy of a salt in J/mol, T is the temperature in Kelvin. For the reaction of

$MgI_2 \cdot 6NH_3$ into $MgI_2 \cdot 2NH_3$ the $\Delta_r H^0_{m \to n} = (74 \pm 3) \cdot 10^1$ kJ/mol $\Delta_r H^0$ at a vapor pressure of 0.9 MPa and a temperature of 613 K [17].

This equation allows to calculate with know decomposition temperatures and pressures the corresponding enthalpy and entropy of reaction $\Delta_r H^0_{m \to n}$ of a salt.

2.1. Literature of ammoniates

We can group the literature about ammoniates:

- **General literature**: [19, 20, 21, 22, 23, 24, 25, 26, 27, 28].
- **Halogenides**: Cl[20, 15, 29, 10, 30, 31, 32, 33, 34, 35, 36, 11, 27, 1, 37, 38, 39, 40, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 17, 50, 51, 52, 13, 2, 16, 53, 54, 55, 56, 57, 58], Br[20, 33, 29, 32, 35, 36, 27, 37, 38, 59, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 17, 50, 51, 52, 14, 54, 55, 57, 60, 58], I [20, 33, 29, 34, 32, 35, 36, 27, 37, 59, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 17, 50, 51, 52, 54, 55, 57, 58] and F [61, 14].
- **Alkali metals**: Li [49, 20, 13, 16, 57, 27]; Na[49, 20, 27, 34]; K [49, 20, 34]; Rb [49, 20, 34] and Cs [49, 20].
- **Alkaline earth metals**: Be [20, 50, 51, 62, 30]; Mg [20, 17, 50, 54]; Ca [20, 63, 2, 1, 27, 35, 10, 31]; Sr [20, 63, 50, 64, 33] and Ba [20, 63, 50, 1, 27, 36].
- **Transition metals (3d)**: Cr [38, 37, 15]; Mn [20, 45, 50, 54, 62, 39, 27]; Fe [20, 45, 50, 54, 62, 39, 37, 27]; Co [20, 45, 50, 14, 54, 62, 39, 59]; Ni [20, 47, 50, 54, 55, 62, 40, 39, 59, 27]; Cu [20, 50, 54, 57, 58, 62, 43, 40, 64, 27, 65, 29] and Zn [20, 54, 44, 62, 42, 40, 39, 64, 10].
- **Other metals**: Pt [37]; Ag [20, 52, 56, 62, 64, 11, 10]; Au [46, 60]; Cd [50, 54, 62, 40, 64]; Hg [50, 61, 62]; Al [53, 37, 32]; In [32]; Tl [20, 37, 29]; Sb [61]; Sn [20, 48, 62] and Pb [20].
- **Sulphates** [62, 43, 42, 59, 37, 65];
- **$NiXO_4$ (X=S; Se; Cr; W or Mo)** [66];
- **Double salts** [48, 60, 67, 65]

2.2. Thermodynamic overview of ammoniates

The pT data from the literature gives the possibility to determine the enthalpy of reaction of various ammoniates, $(\Delta_r H^+ = \Delta_r H^0 \cdot (m - n))$, as a function of the decomposition temperature, T, which is plotted in Figures 2. As can be seen for various loadings of the ammoniates an approximately linear relationship between enthalpy of reaction and dissociation temperature is found for each specific loading and charge combination. Also, a higher loading corresponds to a higher enthalpy of reaction and a lower dissociation temperature. In this graph some reactions have a reaction temperature below the 294 K, the equilibrium temperature of NH_3 at 0.9 MPa. These reactions seems unrealistic and will be indicated as such in Appendix 1.

2.2.1. Selection of salts

Selection of the most suitable salt complex for heat storage from the point of view of energy density, is based on the amount of heat that is stored in the system by removing one ammonia molecule from the salt crystal. In Figure 3, we plotted the enthalpy of reaction stored in a complex divided by the amount of ammonia molecules from a structure $\Delta_r H^0$) plotted against the decomposition temperature for the ammonia pressures at 0.9 MPa (equal to an equilibrium vapor pressure of ammonia at 294 K).
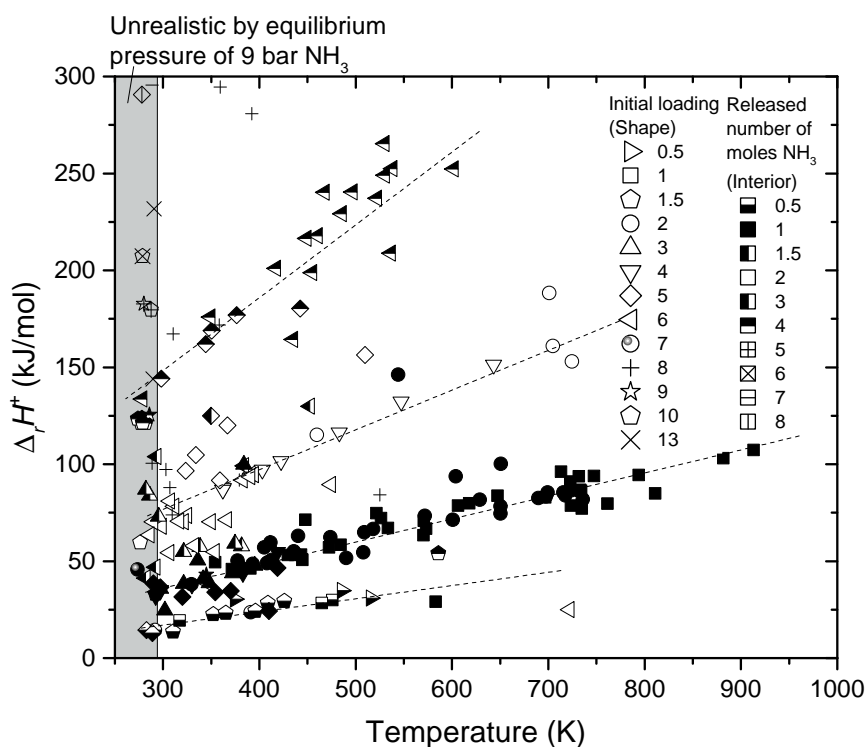
Figure 2. The dissociation temperatures against the calculated enthalpy of reaction ($\Delta_r H^+$) for different loadings with NH$_3$ equilibrated at an ammonia pressure of 0.9 MPa. The symbols of the data points are ordered by the number of moles of ammonia per mole salt and the released number of moles of ammonia in the reaction. The lines are first order guides to the eyes.

The symbols of the data points refer to specific loading and release of ammonia during the reaction. As can be seen a linear trend exists at constant pressure. In the inset, the average enthalpy of reaction is plotted for the four groups, indicating that the alkali metals have the lowest energy stored per added mole ammonia and the transition metals (3d) have the highest amount of energy stored per added mole ammonia. As the difference in average enthalpy of reaction between the metals is smaller than the error bars, no conclusions can be drawn.

In Figure 4, the enthalpy of reaction stored in a complex divided by the number of ammonia molecules is plotted against the number of moles ammonia in a complex. The pressure used for this graph is 0.9 MPa. The averaged $\Delta_r H^0$ decreases from 70 kJ/mol (mono ammoniate) to 30 kJ/mol (octa ammoniate). It is harder to release the last ammonia molecule of a complex than to release one ammonia molecule at higher loadings. We can understand this by the fact that, relatively, the crystal structure is changing more in case of smaller loadings. At the higher loadings (above six NH$_3$ molecules per mole salt) the enthalpy of reaction falls down to almost the level of the enthalpy of reactions of decomposition of ammonia. In general, from the point of view of heat storage, therefore, it will be of interest to select a complex, which totally decomposes at the applied temperature and pressure, with a maximum loading of six ammonia molecules per complex, based on Figure 4.

2.3. Discussion

The operation conditions are a first criteria for selection an ammoniate as TCM. For example in the case of a heating system in houses, the turnover temperature should be between 343 K and 393 K for sufficient charging power with help of solar collectors [68]. In addition, secondly the amount of ammonia per mol salt refines the selection. With a larger loading number, less salt is needed to store all heat, but as already mentioned, a loading above six is not favorable. The final selection criteria is the amount of ammonia, which is lost at the applied temperature. Moreover, thirdly, the equilibrium ammonia pressure of the reaction at temperature of 343–393 K should be in the order of 0.6–1 MPa, what are the equilibrium vapor pressures of ammonia between 283–298 K. This is necessary as the TCM is connected with a storage vessel of ammonia. In case the equilibrium pressure of ammonia of the storage vessel is higher than of the equilibrium pressure of the reaction, the salt will not deammoniate. Or the other way around, in case the equilibrium pressure of the storage vessel is lower that the equilibrium pressure of the reaction, the salt will not ammoniate. As the storage vessel can be kept at a temperature of 283 K in the winter and 298 K in the summer the working pressures are chosen between 0.6–1 MPa.

As in the literature not all decomposition reactions are fully given, only the enthalpy per released mole NH_3 is plotted against the equilibrium temperature between 330–410 K in figure 5. As can be seen
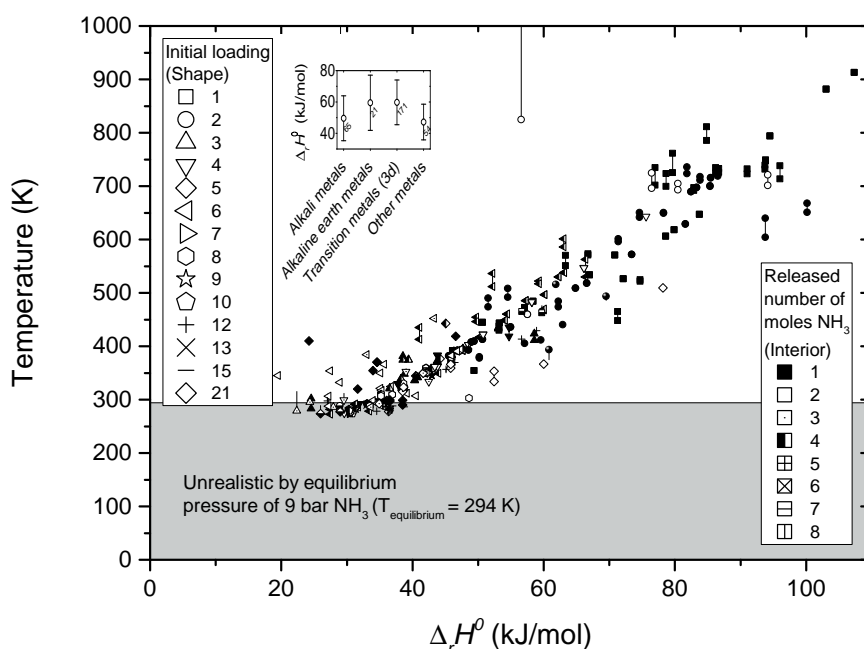
Figure 3. The dissociation temperature of a complex plotted against the enthalpy of reaction stored in a complex divided by the number of ammonia molecules. The ammonia pressure is 0.9 MPa. In the inset the average enthalpy of reaction of the four different groups are plotted, whereby only complexes with maximum loading of 6 are used in this average. The labels correspond to the number of complexes in the data set.
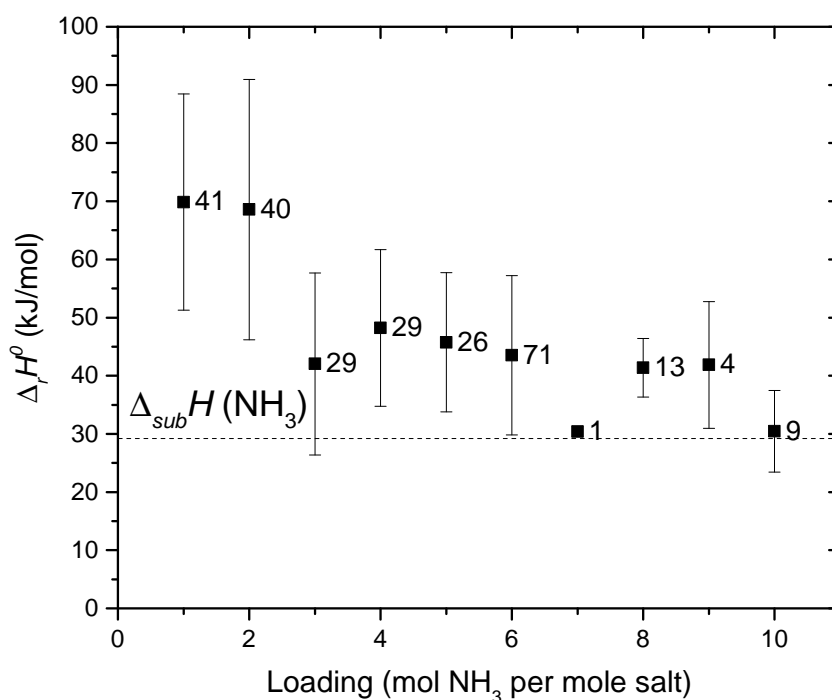
Figure 4. The enthalpy of reaction stored in a complex divided by the number of ammonia molecules plotted against the number of moles ammonia in a complex. The ammonia pressure is 0.9 MPa. The enthalpy of reaction is the average of all groups and the error bar is the standard deviation. The labels correspond to the number of complexes in the data set. The dashed line indicates the heat of sublimation of an ammonia molecule.
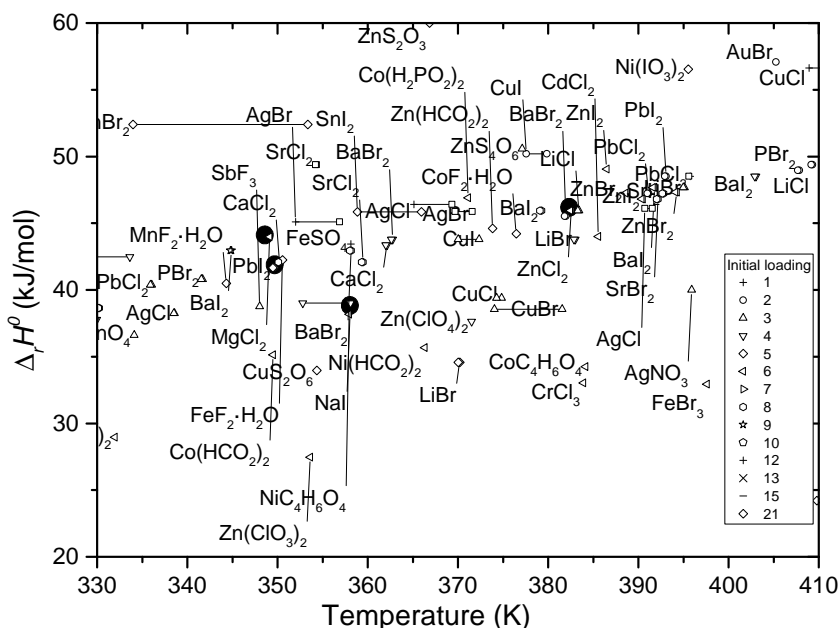
Figure 5. The enthalpy of reaction stored in a complex divided by the number of ammonia molecules plotted against the equilibrium temperature of the complex. The ammonia pressure is 0.9 MPa. The temperature is limited between 330-410 K.

a large range of materials fits the demands. As currently not sufficient data is available a single choice of material can not be made. Based on prices of the future heat storage systems, materials like silver, copper, cesium and lithium are not considered. Based on this data sheet, the most common materials are indicated with a solid sphere ($MgCl_2 \cdot 6NH_3$, $CaCl_2 \cdot 8\text{-}4NH_3$, and $ZnCl_2 \cdot 6NH_3$). In further research other material properties like melting points, densities, deliquescence points and costs should be considered as well. These parameters should be considered before a heat storage system for domestic households based on ammoniates can be designed.

2.4. Concluding remarks

We analyzed a large set of thermodynamic data of ammoniates. For various loadings of ammoniates, the dissociation temperature shows an approximate linear relationship with the enthalpy of reaction. Indeed, by dividing the enthalpy of reaction by the loading, all data points fall on one master curve, which can be divided by the periodic groups. Lower loadings have a large heat storage capacity per molecule of complex, implying that complexes with loading of six or lower are more favorable for heat storage application. With the help of this data set, appropriate ammoniates can be selected as heat storage material for a given temperature and ammonia partial pressure. In the future, before heat storage in domestic environment is feasible, additional research should be performed on melting temperature of certain complexes, deliquescence of the complex, density of the complexes and combined transitions.

2.5. Appendix 1

Salt is the basic salt in the reaction; Initial is the highest loading in the reaction; Final the lowest loading in the reaction; ΔH^0 is the enthalpy of the reaction; ΔS the entropy of the reaction; $T_{p=9bar}$ is the maximum ammoniation temperature by 9 bar ammonia vapor pressure. The used type of thermodynamic data and source is given in column pT/H and in case of *pT* data is used the minimum and maximum temperature of the used *pT* data is given in columns T_{min} and T_{max} and the number of data points used in the next column. If the final loading is unknown, this is indicated with a question mark(?). In case doubts about the reliability of the data is raised, they are indicated with an asterisk *.

Salt	Initial loading (n)	Final loading (m)	ΔH^0 (kJ/mol)	ΔS (J/(mol·K))	$T_{p=0.9MPa}$ (K)	pT/H	T_{min} (K)	T_{max} (K)	Data points	Ref
AgBr	3	1.5	-36.5	132	322	pT	250	276.5	5	[52]
AgBr	1.5	1	-45.1	146	352	pT	273	307	11	[52]
AgBr	1	0	-45.9	142	372	pT	273	324.5	6	[52]
AgBrO$_3$	3	?	-33.9	124	322	pT	252	274.5	4	[56]
AgCl	3	1.5	-38.2	131	339	pT	248	290.8	11	[56, 52]
AgCl	1.5	1	-46.4	145	365	pT	273	305.8	6	[52]
AgCl	1	0	-46.1	136	391	pT	273	336	7	[52]
AgClO$_3$	3	?	-74.6	226	360	pT	284	324.5	3	[56]
AgClO$_4$	3	?	-37.2	105	427	pT	282	352	7	[56]
AgI	3	2	-24.5	100	302	pT	194	314.5	4	[52]
AgI*	2	1.5	-28.9	117	292	pT	194	215.7	2	[52]
AgI	1.5	1	-27.0	105	310	pT	215.7	253	4	[52]
AgI	1	0.5	-38.8	140	317	pT	241	276.5	5	[52]
AgI	0.5	0	-60.8	181	375	pT	292	316.5	3	[52]
AgMnO$_4$	3	?	-36.6	128	334	pT	252	285	5	[56]
AgNO$_2$	3	?	-33.1	96	426	pT	253	341	8	[56]
AgNO$_3$	3	?	-40.0	119	396	pT	273	336	8	[56]
AlBr$_3$	6	?	-48.9	96	627	pT	421	502	5	[37]
AlCl$_3$	6	?	-50.0	123	476	pT	320	401	5	[37]
AlI$_3$	6	?	-45.9	130	413	pT	292.5	353.5	3	[37]
AuBr	6	4	-34.0	132	298	pT	203	233	6	[46]
AuBr	4	3	-34.9	136	297	pT	194.5	233	8	[46]
AuBr	3	2	-35.7	138	298	pT	194.5	233	8	[46]
AuBr	2	1	-57.1	159	405	pT	307	338	5	[46]
AuCl	6	2	-33.4	138	278	pT	194.5	233	7	[46]
AuCl	2	1	-62.9	161	440	pT	307	372.5	7	[46]
AuI*	6	3	-34.7	136	293	pT	194.5	228	7	[46]
AuI	3	2	-38.3	138	321	pT	213	263	10	[46]
AuI	2	1	-38.0	134	329	pT	213	273	9	[46]
BaBr$_2$	8	4	-43.0	138	358	H				[20]
BaBr$_2$	4	2	-43.9	139	363	H				[20]
BaBr$_2$	2	1	-45.6	138	382	H				[20]
BaBr$_2$	1	0	-50.7	132	445	H				[20]
BaCl$_2$	8	?	-38.7	135	330	H				[20]
BaI$_2$*	10	9	-33.1	132	292	H				[20]
BaI$_2$	9	8	-43.0	143	345	H				[20]
BaI$_2$	8	6	-46.0	140	379	H				[20]
BaI$_2$	6	4	-47.7	140	392	H				[20]
BaI$_2$	4	2	-48.6	139	403	H				[20]
BaI$_2$	2	0	-57.6	144	460	H				[20]
BeBr$_2$	10	6	-13.5	41	586	pT	194.5	268	5	[51]
BeBr$_2$	6	4	-39.2	144	312	pT	228	243	4	[51]
BeCl$_2$	12	6	-34.6	142	279	pT	194.5	228	5	[51]
BeCl$_2$	6	4	-35.1	140	289	pT	213	238	6	[51]
BeCl$_2$	4	2	-75.6	136	643	pT	383.7	428.8	3	[51]
BeI$_2$*	13	6	-33.1	132	291	pT	194.5	208	3	[51]
BeI$_2$	6	4	-36.7	131	325	pT	223	243	3	[51]
CaBr$_2$	8	6	-42.1	99	525	H				[20]
CaBr$_2$	6	2	-50.3	139	417	H				[20]
CaBr$_2$	2	1	-73.5	147	572	H				[20]
CaBr$_2$	1	0	-80.0	148	618	H				[20]
CaCl$_2$	8	4	-42.1	139	350	H				[20]
CaCl$_2$	4	2	-43.4	138	362	H				[20]
CaCl$_2$	2	1	-64.9	146	509	H				[20]
CaCl$_2$	1	0	-70.9	143	571	H				[20]
CaI$_2$	8	6	-37.0	138	309	H				[20]
CaI$_2$	6	2	-60.2	139	497	H				[20]
CaI$_2$	2	1	-81.7	148	629	H				[20]
CaI$_2$	1	0	-83.8	148	647	H				[20]
Cd(ClO$_3$)$_2$	6	4	-44.7	113	474	pT	342	395	6	[40]
Cd(ClO$_3$)$_2$	4	?	-71.7	168	478	pT	389.5	409	3	[40]
Cd(IO$_3$)$_2$	4	?	-37.6	97	476	pT	364	383	3	[40]
CdBr$_2$	6	?	-48.3	135	412	pT	318	357.3	8	[54]
CdCl$_2$	6		-44.0	132	386	pT	306.5	330.5	2	[54]
CdI$_2$	6	?	-51.0	134	441	pT	339	381.5	8	[54]

Salt	Initial loading (n)	Final loading (m)	ΔH^0 (kJ/mol)	ΔS (J/(mol·K))	$T_{p=0.9MPa}$ (K)	pT/H	T_{min} (K)	T_{max} (K)	Data points	Ref
Co(H$_2$PO$_2$)$_2$	6	?	-46.9	145	371	pT	293	324	6	[59]
Co(HCO$_2$)$_2$	6	4	-35.1	119	350	pT	258	294.5	7	[59]
Co(HCO$_2$)$_2$	4	?	-44.7	122	432	pT	297	365	7	[59]
Co(NO$_3$)$_2$	6	?	-29.5	65	631	pT	294	433	8	[59]
CoBr$_2$	6	2	-52.2	116	536	pT	409.8	448.5	3	[24]
CoBr$_2$	2	1	-83.8	135	718	pT	425	454.8	3	[24]
CoBr$_2$	1	0	-91.0	144	723	pT	434.4	481.4	4	[24]
CoC$_4$H$_6$Ø$_4$	6	?	-34.2	107	384	pT	273	319	9	[59]
CoCl$_2$*	10	6	-30.3	127	277	pT	194.5	218	5	[24]
CoCl$_2$	6	2	-60.1	147	468	pT	380.5	410	3	[45]
CoCl$_2$*	2	1	-29.0	39	1390	pT	503	509	3	[24]
CoCl$_2$	1	0	-96.0	153	713	pT	481	503	3	[24]
CoF$_2$·H$_2$O	5	1	-44.2	136	376	pT	262	299	5	[61]
CoF$_2$·H$_2$O	1	0	-53.2	140	437	pT	307	334.5	3	[61]
CoI$_2$	6	2	-63.2	136	538	H				[24]
CoI$_2$	2	1	-146.2	287	544	pT	409.5	426.5	2	[24]
CoS$_2$O$_6$	5	?	-51.7	120	509	pT	373.5	430.5	8	[59]
Cr[NH$_3$]$_6$Br	6	?	-89.8	184	541	pT	439	450	2	[37]
Cr[NH$_3$]$_6$I	6	?	-51.3	117	518	pT	345.5	415	3	[37]
Cr[NH$_3$]$_6$NO$_3$Br$_2$	6	?	-75.2	163	519	pT	411.7	459	4	[37]
Cr[NH$_3$]$_6$SO$_4$	6	?	-31.3	68	624	pT	343	444.5	5	[37]
CrCl$_3$	6	3	-33.0	104	384	pT	273	316.5	6	[37]
CrCl$_3$	3	?	-53.7	145	424	pT	317	368	6	[37]
Cu(ClO$_3$)$_2$	6	?	-16.3	52	485	pT	258	304	5	[40]
Cu(ClO$_4$)$_2$	6	?	-31.3	88	447	pT	293	356	9	[43]
Cu(HCOO)$_2$	4	?	-37.9	109	417	pT	260	335	11	[43]
Cu(IO$_3$)$_2$	5	4	-46.6	130	419	pT	323.5	357.5	5	[40]
Cu(NO$_3$)$_2$	4	?	-64.9	136	552	pT	416	448.5	4	[43]
Cu(NO$_3$)$_2$	6	4	-35.1	128	321	pT	255	286	7	[43]
Cu(SCN)$_2$	6	4	-19.5	75	345	pT	254	261	3	[43]
Cu(SCN)$_2$	4	?	-56.6	148	436	pT	290.5	383	10	[43]
CuBr	3	1.5	-38.5	119	382	pT	285	322	7	[57, 17]
CuBr	1.5	1	-58.9	157	426	pT	306	371	4	[17]
CuBr	1	0	-71.3	177	448	pT	317	349.8	3	[17]
CuC$_2$O$_4$	5	?	-64.1	206	341	pT	254	311	8	[43]
CuC$_7$H$_5$O$_7$	5	4	-31.6	117	320	pT	257	270.5	4	[43]
CuCl	1.5	1	-56.6	157	409	pT	305.7	349.3	3	[29]
CuCl	1	0	-74.7	161	522	pT	305.7	349.3	3	[29]
CuCl	6	3	-43.3	114	452	pT	346	378	4	[54]
CuCl	3	1.5	-39.4	123	375	pT	288	320	7	[57]
CuI	3	2	-43.8	136	372	pT	263	322	7	[57, 17]
CuI	2	1	-50.2	151	378	pT	281	317	4	[17]
CuI	1	0.5	-59.7	144	476	pT	349.6	382	3	[17]
CuI	0.5	0	-69.5	161	486	pT	371	409	3	[17]
CuS$_2$O$_6$	5	4	-34.0	114	354	pT	253	299	9	[43]
CuS$_2$O$_6$*	4	?	-20.3	23	3991	pT	385	457	4	[43]
CuS$_4$O$_6$	4	?	-57.0	154	420	pT	293.5	366	6	[43]
FeBr	6	2	-57.4	136	485	H				[20]
FeBr	2	1	-85.4	140	699	pT	488	550	3	[24]
FeBr	1	0	-86.7	137	733	pT	488	550	3	[24]
FeBr$_3$	6	?	-32.9	101	398	pT	273	326	6	[37]
FeCl$_2$*	10	6	-31.0	130	278	pT	194.5	218	5	[45]
FeCl$_2$	6	2	-49.7	128	455	pT	344	387	5	[54, 24]
FeCl$_2$	2	1	-74.6	133	650	pT	503	550	2	[24]
FeCl$_2$	1	0	-79.6	123	761	pT	487.5	550	3	[24]
FeCl$_3$	6	?	-36.8	107	416	pT	300.5	343.5	6	[37]
FeF$_2$·H$_2$O	5	1	-42.3	139	351	pT	252	273	3	[61]
FeF$_2$·H$_2$O	1	0	-53.2	142	430	pT	298	334	4	[61]
FeI$_2$	6	2	-62.3	136	530	H				[20]
FeI$_2$	2	0	-94.2	153	701	pT	488	551	3	[24]
FeSO$_4$	12	?	-43.4	140	358	pT	273	310	7	[37]
InBr$_3$*	15	?	-38.7	153	287	pT	194.5	231.4	4	[69]
InCl$_3$*	15	7	-36.9	146	289	pT	194.5	235.2	5	[69]
InI$_3$*	21	13	-36.3	149	278	pT	194.5	223.4	4	[69]
InI$_3$*	13	9	-36.0	142	290	pT	215.5	233.5	3	[69]
InI$_3$	9	?	-56.6	207	300	pT	244.5	253.1	3	[69]
KBr*	4	?	-29.6	125	278	pT	194.5	213	3	[49]
KI	6	4	-27.2	107	306	pT	194.5	203	2	[49]
KI	4	?	-29.5	113	311	pT	194.5	218	5	[49]
LiBr*	6.5	5	-27.5	116	282	pT	194.5	213	2	[49]
LiBr	5	1	-36.0	139	298	pT	213	253	4	[49]
LiBr	5	4	-34.6	112	370	H				[20]
LiBr	4	3	-43.9	133	383	H				[20]
LiBr	3	2	-47.7	139	395	H				[20]
LiBr	2	1	-50.7	141	413	H				[20]
LiBr	1	0	-58.5	139	484	H				[20]
LiBr	1	?	-57.1	136	487	pT	334	384	5	[49]
LiCl*	5	4	-38.5	151	290	pT	214.5	228	3	[49]
LiCl	4	3	-37.8	133	330	H				[20]

Salt	Initial loading (n)	Final loading (m)	ΔH^0 (kJ/mol)	ΔS (J/(mol·K))	$T_{p=0.9MPa}$ (K)	pT/H	T_{min} (K)	T_{max} (K)	Data points	Ref
LiCl	3	2	-46.0	138	383	H				[20]
LiCl	2	1	-49.4	139	409	H				[20]
LiCl	1	0	-53.3	139	443	H				[20]
LiI*	7	5.5	-30.4	129	274	pT	194.5	213	3	[49]
LiI*	5.5	5	-29.0	121	283	pT	194.5	213	3	[49]
LiI	5	4	-36.6	141	297	pT	203	253	5	[49]
LiI	4	3	-54.7	149	419	pT	288	363.5	12	[49, 57]
LiI	3	2	-53.1	141	433	pT	291	337.8	5	[49]
LiI	2	1	-54.5	126	508	pT	337.8	373	5	[49]
LiI	1	0	-66.7	135	573	pT	388	408	3	[49]
MgBr$_2$	2	1	-81.9	129	736	pT	488	573	4	[17]
MgBr$_2$	1	0	-84.9	123	811	pT	503	573	3	[17]
MgCl$_2$	2	1	-93.8	174	604	pT	458	502	3	[17]
MgCl$_2$	1	0	-93.7	146	732	pT	502	572	3	[17]
MgCl$_2$	6	2	-44.0	144	349	pT	283	303.5	4	[54]
MgI$_2$	6	2	-74.0	136	825	H				[20]
MgI$_2$*	2	0	-56.6	57	1450	pT	488	503	2	[17]
MnBr$_2$	10	6	-30.8	131	274	pT	194.5	218	5	[45]
MnBr$_2$	2	1	-78.3	139	650	pT	455	503	3	[24]
MnBr$_2$	1	0	-78.6	127	724	pT	488	551	3	[24]
MnBr$_2$	6	2	-54.5	137	460	H				[24]
MnCl$_2$*	12	10	-29.8	126	276	pT	194.5	208	2	[45]
MnCl$_2$*	10	6	-30.3	126	282	pT	194.5	223	5	[45]
MnCl$_2$	6	2	-41.1	113	435	pT	332	362	7	[24, 54]
MnCl$_2$	2	1	-71.4	137	601	pT	454	503	3	[24]
MnCl$_2$	1	0	-77.0	123	735	pT	488	551	3	[24]
MnF$_2$·H$_2$O	5	1	-40.5	136	344	pT	252	273	3	[61]
MnF$_2$·H$_2$O	1	?	-53.7	144	426	pT	298	334	4	[61]
MnI$_2$	2	0	-76.5	124	725	pT	481	488	2	[24]
MnI$_2$	6	2	-60.9	136	518	H				[24]
NaBr*	5.75	5.25	-26.0	108	289	pT	194.5	213	3	[49]
NaBr	5.25	?	-38.5	143	309	pT	213	243	4	[49]
NaCl*	5	?	-34.9	140	286	pT	194.5	249	4	[49]
NaI*	6	4.5	-31.3	125	292	pT	194.5	218	6	[49]
NaI	4.5	?	-39.0	127	358	pT	233	273	5	[49]
Ni(C$_7$H$_5$O$_2$)$_2$	8	6	-48.6	179	303	pT	257	271.5	6	[26]
Ni(C$_7$H$_5$O$_2$)$_2$	6	?	-10.7	31	829	pT	288	362	6	[26]
Ni(ClO$_3$)$_2$	6	?	-44.9	90	629	pT	399	432	3	[55]
Ni(CNS)$_2$	6	?	-48.7	136	413	pT	318	357	6	[55]
Ni(H$_2$PO$_2$)$_2$	6	?	-50.1	137	422	pT	313	368	5	[55]
Ni(HCO$_2$)$_2$	6	4	-35.7	116	366	pT	273	308	8	[55]
Ni(HCO$_2$)$_2$	4	?	-61.1	145	483	pT	333	413	5	[55]
Ni(IO$_3$)$_2$	5	?	-56.5	161	396	pT	326	352	4	[40]
Ni(NO$_2$)$_2$	5	?	-37.6	97	479	pT	320.5	388	9	[55]
Ni(NO$_3$)$_2$	6	?	-47.4	101	569	pT	388	464	13	[55]
NiBr$_2$	6	2	-66.4	144	530	pT	429	460	2	[54]
NiBr$_2$	2	1	-86.6	138	725	pT	491	629	22	[24]
NiBr$_2$	1	0	-86.2	136	734	pT	549	609	3	[24]
NiC$_4$H$_6$O$_4$	6	?	-38.2	125	358	pT	273	306	7	[59]
NiCl$_2$	6	2	-59.3	132	522	pT	403	448	5	[54, 47]
NiCl$_2$	2	1	-100.1	172	651	pT	488	584	7	[47]
NiCl$_2$	1	0	-93.8	144	747	pT	538	646	7	[47]
NiF$_2$·H$_2$O	5	1	-45.1	120	442	pT	273	334.5	5	[61]
NiF$_2$·H$_2$O	1	?	-55.0	143	442	pT	307.5	334	3	[61]
NiI$_2$	6	2	-63.1	123	601	pT	447	491	3	[47]
NiI$_2$	2	0	-80.5	132	705	pT	452	595.5	12	[47]
NiS$_2$O$_3$	5	?	-55.9	134	482	pT	364.5	415	6	[55]
NiS$_2$O$_6$	6	?	-47.2	102	562	pT	389	455.5	7	[55]
NiS$_4$O$_6$	6	?	-52.8	130	472	pT	349	404.5	7	[55]
PbCl$_2$	8	3.25	-35.3	132	310	H				[20]
PbCl$_2$	3.25	2	-40.4	139	336	H				[20]
PbCl$_2$	2	1.5	-47.3	139	391	H				[20]
PbCl$_2$	1.5	1	-48.6	141	396	H				[20]
PbCl$_2$	1	0	-57.2	139	472	H				[20]
PbI$_2$*	8	5	-33.5	135	288	H				[20]
PbI$_2$	5	2	-41.7	138	349	H				[20]
PbI$_2$	2	1	-48.6	142	393	H				[20]
PbI$_2$	1	0.5	-56.8	140	465	H				[20]
PbI$_2$	0.5	0	-61.9	138	516	H				[20]
PBr$_2$	8	5.5	-35.3	133	307	H				[20]
PBr$_2$	5.5	3	-38.7	138	323	H				[20]
PBr$_2$	3	2	-40.8	138	342	H				[20]
PBr$_2$	2	1	-49.0	138	408	H				[20]
PBr$_2$	1	0	-67.1	144	534	H				[20]
PtCl$_3$	5	4	-24.2	77	410	pT	259	314.5	9	[37]
PtI$_3$	6	4	-40.5	150	307	pT	265	267.5	3	[37]
PtI$_3$	4	?	-59.0	133	514	pT	399	436	2	[37]
RbBr	3	?	-22.4	89	315	pT	194.5	203	2	[49]
RbI*	6	?	-33.6	139	279	pT	194.5	203	2	[49]

Salt	Initial loading (n)	Final loading (m)	ΔH^0 (kJ/mol)	ΔS (J/(mol·K))	$T_{p=0.9MPa}$ (K)	pT/H	T_{min} (K)	T_{max} (K)	Data points	Ref
SbF$_3$*	6	4	-31.7	129	286	pT	194.5	223	5	[61]
SbF$_3$*	4	3	-31.9	127	292	pT	213	223	3	[61]
SbF$_3$	3	2	-38.8	130	348	pT	252	273	3	[61]
SbF$_3$	2	1	-59.6	163	412	pT	290	335	4	[61]
SbF$_3$	1	?	-59.7	140	489	pT	334.5	383	5	[61]
SnBr$_2$*	9	5	-31.4	128	286	pT	194.5	233.3	3	[?]
SnBr$_2$	5	3	-52.4	175	334	pT	251.7	290.6	3	[?]
SnBr$_2$	3	2	-99.9	278	384	pT	328.9	337.6	3	[?]
SnBr$_2$	2	1	-62.2	150	474	pT	353	383.5	3	[?]
SnBr$_2$	1	0	-85.1	141	692	H				[20]
SnCl$_2$	9	4	-36.5	149	280	pT	194.5	236.4	3	[?]
SnCl$_2$	4	?	-42.5	148	328	pT	237	283.6	3	[?]
SnI$_2$*	10	5	-35.9	143	288	pT	194.5	227	3	[?]
SnI$_2$	5	3	-45.8	146	359	pT	250	289.5	3	[?]
SnI$_2$	3	2	-58.6	161	411	pT	307.8	353	3	[?]
SnI$_2$	2	1	-51.5	123	490	pT	334	370	3	[?]
SnI$_2$	1	0	-63.3	129	570	pT	370	412	3	[?]
SrBr$_2$	8	2	-46.9	138	392	H				[20]
SrBr$_2$	2	1	-55.0	145	436	H				[20]
SrBr$_2$	1	0	-72.2	156	526	H				[20]
SrCl$_2$	8	1	-42.1	136	359	H				[20]
SrCl$_2$	1	0	-49.4	158	354	H				[20]
SrI$_2$	8	6	-47.3	139	393	H				[20]
SrI$_2$	6	2	-54.2	139	449	H				[20]
SrI$_2$	2	1	-66.6	147	518	H				[20]
SrI$_2$	1	0	-78.7	148	606	H				[20]
Tl(SO$_4$)$_3$	10	?	-38.6	104	453	pT	333	373	3	[37]
TlBr	3	0	-24.4	101	296	pT	213	223	2	[17]
TlCl*	3	0	-27.9	116	286	pT	194	223	3	[17]
TlCl$_3$	6	?	-36.9	97	469	pT	294.5	374	5	[37]
TlI*	3	0	-29.0	121	282	pT	194	223	3	[17]
Zn(ClO$_3$)$_2$	6	?	-36.7	63	829	pT	387	450	4	[54]
Zn(ClO$_3$)$_2$	6	4	-27.5	96	354	pT	258	284	13	[40]
Zn(ClO$_4$)$_2$	4	?	-37.6	120	372	pT	265	315	9	[40]
Zn(CNS)$_2$	4	?	-57.7	158	414	pT	304	361	9	[42]
Zn(CNS)$_2$	6	4	-28.9	105	332	pT	252	273	3	[42]
Zn(HCO$_2$)$_2$	5	?	-44.6	138	374	pT	281	324	9	[42]
Zn(IO$_3$)$_2$	4	?	-46.4	109	513	pT	350	403	5	[40]
Zn(NO$_2$)$_2$	1	0	-29.1	68	583	pT	298	401	15	[42]
Zn(NO$_3$)$_2$	6	4	-12.5	36	722	pT	273	356	8	[42]
Zn(NO$_3$)$_2$	4	?	-54.5	110	593	pT	380	481	12	[42]
ZnBr$_2$	6	?	-47.2	140	389	pT	285	339.5	13	[54]
ZnBr$_2$	6	4	-47.4	138	394	H				[20]
ZnBr$_2$	4	2	-58.3	139	483	H				[20]
ZnBr$_2$	2	1	-85.6	138	715	H				[20]
ZnBr$_2$	1	0	-103.2	135	881	H				[20]
ZnC$_2$H$_2$O$_4$	5	?	-49.2	169	327	pT	256	288	9	[42]
ZnC$_7$H$_6$O$_2$	6	4	-35.3	130	317	pT	253	270	4	[42]
ZnCH$_3$OOH	2	?	-98.2	232	459	pT	377	421	10	[42]
ZnCl$_2$*	10	6	-30.4	127	279	H				[20]
ZnCl$_2$	6	4	-46.0	139	382	H				[20]
ZnCl$_2$	4	2	-50.8	139	423	H				[20]
ZnCl$_2$	2	1	-82.6	138	689	H				[20]
ZnCl$_2$	1	0	-107.5	136	913	H				[20]
ZnI$_2$	6	?	-49.1	145	387	pT	284	340	20	[54, 42]
ZnI$_2$	6	4	-46.9	138	390	H				[20]
ZnI$_2$	4	2	-66.2	139	547	H				[20]
ZnI$_2$	2	1	-83.4	138	697	H				[20]
ZnI$_2$	1	0	-94.6	137	794	H				[20]
ZnS$_2$O$_3$	5	3	-60.0	182	367	pT	288	332	6	[42]
ZnS$_2$O$_3$	3	?	-32.8	70	631	pT	337	445	10	[42]
ZnS$_2$O$_6$	5	?	-62.6	182	381	pT	297	342	8	[42]
ZnS$_4$O$_6$	5	3	-78.2	172	510	pT	382	450	6	[42]
ZnS$_4$O$_6$	3	?	-50.6	152	377	pT	275	333	12	[42]
ZnSO$_3$	3	?	-42.6	108	476	pT	325	387	7	[42]

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Conflict of Interest

All authors declare no conflict of interest in this paper.

References

1. Goldstein M (1961) Some physical chemical aspects of heat storage. In: *UN Conf on New Sources of Energy* Rome, 411-417.

2. Carling R (1981) Dissociation pressures enthalpies of reaction in $MgCl_2 \cdot H_2O$ and $CaCl_2 \cdot nNH_3$. *J Chem Thermodyn* 13: 503-512.

3. ACGIH (2012) Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices, American Conference of Governmental Industrial Hygienists.

4. Yaws C (2001) *Matheson Gas Data Book* 7th ed., New York : McGraw-Hill.

5. Zabetakis M (1965) Flammability Characteristics of Combustible Gases and Vapors, U.S. Dept of the Interior, bureau of Mines.

6. Posern K, Kaps C (2008) Humidity controlled calorimetric investigation of the hydration of $MgSO_4$ hydrates. *J Therm Anal Calorim* 92(3): 905-909.

7. Offenhartz P, Brown F, Mar R, et al. (1980) A Heat Pump and Thermal Storage System for Solar Heating and Cooling Based on the Reaction of Calcium Chloride and Methanol Vapor. *J Sol Energ* 102(1): 59-65.

8. N'Tsoukpoe, K, Liu H, Le Pierrs, et al. (2009) A review on long-term sorption solar energy storage. *Renew Sust Energ Rev* 13(9): 2385-2396.

9. Becker R, Hartwig H, Köppe H, et al. (1978) *Gmelin Handbuch der Anorganischen Chemie* R. Warncke, 8th ed., Berlin, Heidelberg: Springer Berlin Heidelberg.

10. Isambert M (1868) Recherches sur la dissociation de certains chlorures ammoniacaux. *Cr Hebd Acad Sci* 66: 1259-1262.

11. Horstmann A (1876) Zur Dissociationslehre. *Ber Dtsch Chem Ges* 9(1): 749-758.

12. Nernst W (1969) The new heat theorem, Dover Publications Inc.

13. Bonnefoi J (1901) Compounds of the lithium halides with ammonia. *Ann Chim Phys* 23: 317.

14. Clark G, Buckner H (1922) The properties of subsidiary valence groups. III. The preparation, properties and molecular volume relationships of the hydrates and ammines of cobalt fluoride, bromide, iodide, nitrate, carbonate and citrate. *J Am Chem Soc* 22: 230-244.

15. Schlesinger H, Hammond S (1933) The Ammines of Chromous Chloride. *J Amer Chem Soc* 55(10): 3971-3976.

16. Collins S, Cameron F (1927) Lithium chloride ammonia complexes. *J Phys Chem* 32(11): 1705-1716.

17. Biltz W, Hüttig G (1921) Beiträge zur systematischen Verwandtschaftslehre. XIV. Über die Ammoniakate der Magnesiumhalogenide. *Z Anorg Chem* 119(1): 115-131.

18. Glasser L (2014) Thermodynamics of inorganic hydration and of humidity control, with an extensive database of salt hydrate pairs. *J Chem Eng Data* 59(2): 526-530.

19. Touzain P (1999) Thermodynamic values of ammonia-salts reactions for chemical sorption heat pumps. In Proc. *Int Heat Pump Conf* 225-238.

20. Biltz W (1923) Beiträge zur systematischen Verwandtschaftslehre XXIV. Über das Vermögen kristallisierter Salze, Ammoniak zu binden. *Z Anorg Chem* 130(1): 93-139.

21. Biltz W (1930) Über Molekular- und Atomvolumina. 29. Drei Ordnungsprinzipien des Volumensates der festen Stoffe. *Z Anorg Chem* 193(1): 321-350.

22. Biltz W, Birk E (1924) Über die Koppsche Volumenregel bei kristallisierten Stoffen und Über "gleichraumige" Komplexverbindungen. *Z Anorg Chem* 134(1): 125-136.

23. Biltz W , Grimm H (1925) Über die Gitterenergieen von Ammoniakaten. *Z Anorg Chem* 145(1): 63-87.

24. Biltz W , Hüttig G (1919) Über die Auswertung von Dissoziationsmessungen bei Ammoniakaten nach dem Theorem von Nernst mit Hilfe von Nomogrammen. *Z Anorg Chem* 109(1): 111-125.

25. Ephraim F (1915) Über die Natur der Nebenvalenzen. IX. Über den Einfluss der Stellung des Neutralteils im MolekÜl auf seine Haftfestigkeit. *Ber Dtsch Chem Ges* 48(1): 624-629.

26. Ephraim F (1918) Über die Natur der Nebenvalenzen. XVIII. Octammine. - Volumwirkung des Anions. *Ber Dtsch Chem Ges* 51(1): 644-669.

27. Hart A , Partington J (1943) Dissociation pressures of compounds of ammonia and trideuterammonia with some metallic salts. *J Chem Soc (Resumed)* 104-118.

28. Klemm W, Clausen E , Jacobi H (1931) Beiträge zur systematischen Verwandtschaftslehre. 55. Über die konstitution der Aluminiumhalogenid - Ammoniakate. II. Monammine als "Anlagerungsverbindungen." *Z Anorg Chem* 200(1): 367-384.

29. Stollenwerk W, Biltz W (1921) Beiträge zur systematischen Verwandtschaftslehre. XIII. Über die Ammoniakate der Cupro- und Thallohalogenide. *Z Anorg Chem* 119(1): 97-114.

30. Mieleitner K , Steinmetz H (1913) Über das Hydrat und das Ammoniakat des Berylliumchlorids. *Z Anorg Chem* 80(1): 71-78.

31. Lourdudoss S, Schuler T, Raldow W (1981). Determination of the Heat Capacity of Calcium Chloride Octa- and Tetraammines. *Inorg Chim Acta* 54: 31-33.

32. Klemm W, Tanke E (1931) Beiträge zur systematischen Verwandtschaftslehre. 54. Über die konstitution der Aluminiumhalogenid-Ammoniakate. I. *Z Anorg Chem* 200(1): 343-366.

33. Hüttig G (1922) Beiträge zur systematischen Verwandtschaftslehre. XVIII. Über die Ammoniakate der Strontiumhalogenide. *Z Anorg Chem* 124(1): 322-332.

34. Hüttig, G , Härtl E (1955) Die Adsorptions-Affinität der Alkalihalogenide zu Ammoniak. *Z Anorg Chem* 282(1-6): 110-120.

35. Hüttig G (1922) Beiträge zur systematischen Verwandtschaftslehre. XVI. Über die Ammoniakate der Calciumhalogenide. *Z Anorg Chem* 123(1): 31-42.

36. Hüttig, G, Martin W (1922) Beiträge zur systematischen Verwandtschaftslehre. XIX. Über die Ammoniakate der Bariumhalogenide. *Z Anorg Chem* 125(1): 269-280.

37. Ephraim F , Millmann S (1917) Uber die Natur der Nebenvalenzen. XIV. Der einfluss der Wertigkeit auf die Nebenvalenz-Energie. *Ber Dtsch Chem Ges* 50(1): 529-541.

38. Ephraim F , Zapata C (1934) Über ammoniakate von Chromverbindungen. *Helv Chim Acta* 26(34): 287-295.

39. Ephraim F , Linn R (1913) Über die Natur der Nebenvalenzen. VI. Der Einfluss des Neutralteils auf die Bestandigkeit von Komplexen*Ber Dtsch Chem Ges* 46(3): 3742-3762.

40. Ephraim F , Jahnsen A (1915) Über die Natur der Nebenvalenzen. VIII. Beständigkeit der Ammoniakte von Chloraten, Bromaten und Jodaten. - Thermische Dissoziation und Explosion. *Ber Dtsch Chem Ges* 48(1): 41-56.

41. Ephraim F , Hochuli E (1915) Über die Natur der Nebenvalenzen. X. Beständigkeitsgrenzen komplexer Anionen. II. *Ber Dtsch Chem Ges* 48(1): 629-637.

42. Ephraim F , Bolle E (1915) Über die Natur der Nebenvalenzen. XI. Ammoniakate des Zinks. *Ber Dtsch Chem Ges* 48(1): 638-648.

43. Ephraim F , Bolle E (1915) Über die natur der Nebenvalenzen. XII.: Ammoniakate des Kupfers. *Ber Dtsch Chem Ges* 48(2): 1770-1777.

44. Ephraim F (1919) Über die Natur der Nebenvalenzen. XXIII. Thermischer Abbau von Ammoniakaten des Zinks. *Ber Dtsch Chem Ges* 52(5): 957-964.

45. Biltz W (1925) Beiträge zur systematischen Verwandtschaftslehre XXXII. Höhere Ammoniakate von Halogeniden aus der Eisengruppe. *Z Anorg Chem* 148(1): 145-151.

46. Biltz W (1925) Beiträge zur systematischen Verwandtschaftslehre XXXV. Über Ammoniakate der Aurohalogenide. *Z Anorg Chem* 148(1): 192-206.

47. Biltz W , Fetkenheuer B (1913) Über Ammoniakverbindungen der Nickelhalogenide. *Z Anorg Chem* 83(1): 163-176.

48. Biltz W, Fischer W (1923) Beiträge zur systematischen Verwandtschaftslehre. XXI. Über Ammoniakate der Halogenide des zweiwertigen Zinns. *Z Anorg Chem* 162(1): 1-14.

49. Biltz W, Hansen W (1923) Beiträge zur systematischen Verwandtschaftslehre XX. Über Ammoniakate der Alkalimetallhalogenide. *Z Anorg Chem* 127(1): 1-33.

50. Biltz W, Klatte K, Rahlfs (1927) Beiträge zur systematisch Verwantschaftslehre. XLIV. Varia aus der Chemie der Ammoniakate und Pyridinverbindungen. *Z Anorg Chem* 166(1): 339-350.

51. Biltz W, Messerknecht C (1925) Beiträge zur systematischen Verwandtschaftslehre XXXIII. Über Die Ammoniakate der Berylliumhalogenide. *Z Anorg Chem* 148(1): 157-169.

52. Biltz W, Stollenwerk W (1920) BeitrÜge zur systematischen verwandtschaftslehre. XI. Über halogensilberammoniakate. *Z Anorg Chem* 114(1): 174-202.

53. Cyvin S, Cyvin B, Hargittai I (1974) Spectroscopic studies of the $AlCl_3 \cdot NH_3$ complex. *J Mol Struct* 23: 385-397.

54. Ephraim F (1912) Uber die Natur der Nebenvalenzen. Erste mitteilung: Metallammoniak-Verbindungen. *Ber Dtsch Chem Ges* 45(1): 1322-1331.

55. Ephraim F (1913) Über die Natur der Nebenvalenzen. V.: Der Einfluss des Anions auf die Bestandigkeit komplexer Kationen. *Ber Dtsch Chem Ges* 46(3): 3103-3113.

56. Ephraim F (1918) Über die Natur der Nebenvalenzen. XIX. Ammoniakate des Silbers. *Ber Dtsch Chem Ges* 51(1): 706-710.

57. Ephraim F (1918) Über die Natur der Nebenvalenzen. XX.: Ammoniakate von Cupro- und Lithiumsalzen. *Ber Dtsch Chem Ges* 52(2): 236-241.

58. Ephraim F (1919) Uber die Natur der Nebenvalenzen XXII. Thermischer Abbau von Ammoniakaten des Kupfers. *Ber Dtsch Chem Ges* 52(5): 940-957.

59. Ephraim F , Rosenberg E (1917) Über die Natur der Nebenvalenzen. XVII: Vorausberechnung der Zersetzungstemperaturen von Ammoniakaten. *Ber Dtsch Chem Ges* 51(1): 130-136.

60. Ephraim F (1918) Über die Natur der Nebenvalenzen. XXI.: Goldverbindungen; Ammoniakate von Doppelsalzen: thermischer Zerfall von Doppelhalogeniden. *Ber Dtsch Chem Ges* 52(2): 241-254.

61. Biltz W, Rahlfs E (1927) Beiträge zur systematischen Verwandtschaftslehre. XLV. Über Reaktionsermoglichung durch Gitterweitung und uber Ammoniakate der Fluoride. *Z Anorg Chem* 166(1): 351-376.

62. Ephraim F (1926) Über die ammoniakate von Metalsulfaten. *Ber Dtsch Chem Ges* 59(6): 1219-1231.

63. Biltz W, Hüttig G (1920) Beiträge zur systematischen Verwandtschaftslehre. XII. Über die Verbindingen von Ammoniak mit metallischem Calcium, Strontium und Barium. *Z Anorg Chem* 114(1): 241-265.

64. Ephraim F , Zapata C (1934) Über Ammoniakate von Chromaten und von Perchloraten. *Helv Chim Acta* 17(1): 296-308.

65. Kurnakow N (1895) Uber die zusammengesetzten Metallbasen. Zweite Abhandlung. *J Prakt Chem* 52(1): 490-528.

66. Ephraim F , MÜller F (1921) Über die Natur der Nebenvalenzen, XXV.: Stabilität komplexer Kationen bei wechselnder Grösse der Anionen. *Ber Dtsch Chem Ges* 54(5): 973-978.

67. Spacu G, Spacu P (1933) Über die existenz der Doppelsalzammoniakate. *Z Anorg Chem* 214(2): 113-142.

68. Trier D (2012) Solar district heating guidelines- Solar collectors, Technical report.

69. Klemm W (1927) Die Ammoniakate der Indiumhalogenide. *Z Anorg Allg Chem* 163: 240-252.