J Therm Anal Calorim (2011) 105:13–26
DOI 10.1007/s10973-011-1514-9

Interactions of ammonium nitrate with different additives

Thermodynamic analysis

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Niinistö"s Special Chapter

Abstract In order to elucidate the influence of Ca and Mg carbonates with or without the presence of boron, manganese and copper compounds on the thermal stability of ammonium nitrate (AN), thermodynamic analysis of different reactions between AN and additives was carried out. Temperature dependency of Gibbs free energy changes ΔG_T and equilibrium composition of reaction products were calculated for a set of reactions using the HSC software. Main solid compounds that can form in the systems of AN and carbonates, were $Ca(NO_3)_2$ and $Mg(NO_3)_2$, $Ca(OH)_2$ and $Mg(OH)_2$, CaO_2 and MgO_2, CaO and MgO, and N-containing gaseous compounds NO, N_2O and NO_2. As a result of H_3BO_3, MnO_2 and $CuSO_4$ addition, the content of CuO, Cu_2O and MnO as solids and SO_2, SO_3 and HBO as gaseous reaction products reached the same level. Thereby, their equilibrium concentrations did not depend on the carbonate origin of $CaCO_3$, $MgCO_3$ or $CaMg(CO_3)_2$. Small amount of $CuSO_4$, H_3BO_3 or MnO_2 additive (0.01–0.05 mol) in the system, practically, did not influence the temperature dependencies of ΔG_T of the reactions between AN and $CaCO_3$ or $CaMg(CO_3)_2$. The influence of additives taken in the larger amount (0.5 mol) was evident and, depending on the additive and reaction, shifted their proceeding temperatures in either direction by more than 300–400 K.

Keywords Thermodynamic analysis · Thermodynamic equilibrium · Ammonium nitrate · Calcium carbonate · Magnesium carbonate

Introduction

Ammonium nitrate is the main nitrogen fertilizer used in agriculture because of its high nitrogen content (35%), full solubility in water and relatively simple manufacturing technology [1, 2]. However, the thermal instability of AN requires definite precautions in its storing, transportation and handling [3, 4]. Exothermic decomposition of AN can be expressed by the following generalized reaction equation (i) [4]:

$$NH_4NO_3(s) \leftrightarrows N_2O(g) + 2H_2O(g) \qquad \text{(i)}$$

Using combined TG-DTA-FTIR techniques, it was previously found that limestone and dolomite additives stabilize AN because of the interactions between AN and Ca, Mg carbonates with the formation of Ca, Mg nitrates excluding exothermic explosive decomposition of AN [5, 6]. In order to increase the nutritional value of fertilizers, it is possible to mix them with microelements needed for plants. Boron, manganese and copper deficiency is widely met in Estonian soils [7]. So, in this article, the influence of H_3BO_3, MnO_2 and $CuSO_4$ additives on the thermal behaviour of AN mixed with limestone and/or dolomite has been estimated using thermodynamic calculations as a tool before TA-FTIR measurements.

Thermodynamic calculations

Thermodynamic analysis of interactions between substances provides composition of the equilibrium system at different

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temperatures and different concentrations of the initial compounds, which is required in establishing reactions responsible for the interaction. In isolated reversible systems at constant pressure and temperature, the equilibrium criterion is expressed by the minimum of Gibbs energy. Using the HSC software [8], chemical processes in complex systems can be predicted, based on thermodynamic analysis of equilibrium compositions. The HSC built-in database [8] containing thermodynamic data of more than 15000 species collected from different articles and databases was used as the source for thermodynamic properties of the substances involved in the equilibrium systems studied.

The thermodynamic analysis results can differ from experimental data because this analysis does not count the time required to establish the equilibrium state. However, these results allow to predict thermodynamic probability of the chemical reactions of interest under certain conditions.

Here, thermodynamic analysis of different reactions between AN and additives was carried out to elucidate the influence of Ca, Mg carbonates with or without the presence of boron, manganese and copper compounds on the thermal behaviour of AN. The temperature dependency of Gibbs free energy changes ΔG_T and equilibrium composition of reaction products were calculated for a set of reactions (Table 1). Calculations were based on the AN/carbonates/copper, boron or manganese additive stoichiometry 2/1/0.01, 2/1/0.05 or 2/1/0.5. The amount of carbonates was varied from 0.2 to 2.1 mol with a step of 0.1. The values of ΔG_T were calculated in the temperature range of 273–2073 K.

Results and discussion

Equilibrium in the multi-component system based on AN–$CaCO_3$/$MgCO_3$/$CaMg(CO_3)_2$

Calculations were based on the initial amounts of 2 mol of AN and 1 mol of $CaCO_3$(s) or $MgCO_3$(s) or 0.5 mol $CaMg(CO_3)_2$(s).

The list of the main compounds and their concentrations in equilibrium (Fig. 1) as well as their variations depending on the temperature do not depend much on the origin of carbonate–$CaCO_3$(s), $MgCO_3$(s) or $CaMg(CO_3)_2$(s) being quite similar in the case of each. One can see that a rapid decrease in the content of $Mg(NO_3)_2$(s) and $Ca(NO_3)_2$(s), with the simultaneous increase in the amount of different N-containing gaseous compounds in the system occurs at temperatures up to 673–773 K. The equilibrium content of most of these gaseous compounds continues to increase with the temperature growth up to 2073 K, but the equilibrium amount of many of them e.g. NH(g), NH_2(g), NH_3(g) is small and hardly exceeds the 10^{-10} mol level at temperatures higher than 1573–1773 K. The content of N_2O(g) and HNO_2(g) reach to 10^{-7} mol level at 1273–1373 K, HNO(g) at 1975 K; NO_2(g) reach to 10^{-5} mol at 773–873 K and NO(g) at 673–773 K gaining the 10^{-2}–10^{-1} mol level at 2073 K.

The same changes can be followed after the increase in the content of $Mg(OH)_2$(s) and $Ca(OH)_2$(s) at temperatures up to 500–600 K and 800–1000 K, respectively. Here, the content of Ca, Mg-carbonates and -hydroxides starts to decrease with temperature resulting in the formation and increase in the content of solid CaO_2, MgO_2, CaO and MgO and gaseous CO, CO_2, HO, H_2. The content of gaseous compounds like O_2, N_2 and H_2O does not change in the temperature interval from 273 K to 2073 K.

It can be seen in the equilibrium diagrams of AN with Ca, Mg-carbonates as well as of AN with CaO(s) or MgO(s) that the content of NO_2(g) and N_2O(g) in equilibrium differed slightly (6–7%) as compared to their content in the case of pure ammonium nitrate, thereby, the NO(g) content does not differ at all (Table 2).

At constant temperature and while keeping the amount of AN constant on the level of 2 mol, the equilibrium amount of gaseous compounds does not depend on the content of carbonates varied between 0.2 and 2.1 mol.

Equilibrium in the multi-component system based on AN–$CaCO_3$/$CaMg(CO_3)_2$–Cu, B, Mn additives at the mole ratio of 2:1/0.5:0.01 and 2:1/0.5:0.05

$CuSO_4$

In the systems with $CuSO_4$(s) additive it can be seen that in addition to nitrogen-containing gases also sulphur-containing gaseous compounds like H_2S, HS, SO, SO_2 and SO_3 are present in the equilibrium mixture (Fig. 2, Table 3). The content of nitrogen-containing gases does not depend on the content of $CuSO_4$(s) (whether 0.01 or 0.05 mol) in the system. The content of sulphur-containing gases is proportionally higher at higher content of $CuSO_4$(s) (Table 3).

Comparing the systems with $CuSO_4$(s) additive based on AN with and without carbonates, there are no differences in the content of NO(g) in gaseous phase in the temperature interval from 373 to 2073 K. The content of NO_2(g) and N_2O (g) is on the same level at lower temperatures, but in the systems with carbonates, the increase in temperature is accompanied by the decrease in the content of both gases of about 7–8% (Table 3).

At lower temperatures up to 773–873 K the amount of SO_2(g) and SO_3(g) in equilibrium is 10^{-15}–10^{-19} mol in the system of AN with carbonates, and 10^{-3}–10^{-5} mol without carbonates. The content of SO(g) is 10^{-34}–10^{-35} mol and 10^{-21} mol, respectively, in the system with or without carbonates. At intermediate temperatures between

Table 1 List of reactions

$2NH_4NO_3(s) \leftrightarrows 2N_2O(g) + 4H_2O(g)$ (1)
$2NH_4NO_3(s) + CaCO_3(s) \leftrightarrows Ca(NO_3)_2(s) + CO_2(g) + N_2(g) + H_2O(g) + 3H_2(g)$ (2)
$2NH_4NO_3(s) + CaCO_3(s) \leftrightarrows Ca(NO_3)_2(s) + CO_2(g) + NO(g) + 0.5N_2(g) + 4H_2(g)$ (3)
$2NH_4NO_3(s) + CaCO_3(s) \leftrightarrows Ca(OH)_2(s) + CO_2(g) + 4NO(g) + H_2O(g) + 2H_2(g)$ (4)
$2NH_4NO_3(s) + CaCO_3(s) \leftrightarrows Ca(OH)_2(s) + CO_2(g) + 2NO(g) + N_2(g) + 3H_2O(g)$ (5)
$2NH_4NO_3 + CaCO_3 \leftrightarrows CaO_2 + CO_2(g) + 4NO(g) + H_2O(g) + 3H_2(g)$ (6)
$2NH_4NO_3 + CaCO_3 \leftrightarrows CaO_2 + CO_2(g) + 2NO(g) + N_2(g) + 3H_2O(g) + H_2(g)$ (7)
$2NH_4NO_3 + CaCO_3 \leftrightarrows CaO + CO_2(g) + 4NO(g) + 2H_2O(g) + 2H_2(g)$ (8)
$2NH_4NO_3 + CaCO_3 \leftrightarrows CaO + CO_2(g) + 2NO(g) + N_2(g) + 4H_2O(g)$ (9)

$2NH_4NO_3 + CaCO_3 \leftrightarrows Ca(NO_3)_2 + CO_2(g) + N_2(g) + H_2O(g) + 3H_2(g)$ (10)
$2NH_4NO_3 + CaCO_3 \leftrightarrows Ca(NO_3)_2 + CO_2(g) + 0.5NO_2(g) + 0.75N_2(g) + 4H_2(g)$ (11)
$2NH_4NO_3 + CaCO_3 \leftrightarrows Ca(OH)_2 + CO_2(g) + 2.5NO_2(g) + 0.75N_2(g) + 3H_2(g)$ (12)
$2NH_4NO_3 + CaCO_3 \leftrightarrows Ca(OH)_2 + CO_2(g) + 2NO_2(g) + N_2(g) + H_2O(g) + 2H_2(g)$ (13)
$2NH_4NO_3 + CaCO_3 \leftrightarrows CaO_2 + CO_2(g) + 2.5NO_2(g) + 0.75N_2(g) + 4H_2(g)$ (14)
$2NH_4NO_3 + CaCO_3 \leftrightarrows CaO_2 + CO_2(g) + 2NO_2(g) + N_2(g) + H_2O(g) + 3H_2(g)$ (15)
$2NH_4NO_3 + CaCO_3 \leftrightarrows CaO + CO_2(g) + 3NO_2(g) + 0.5N_2(g) + 4H_2(g)$ (16)
$2NH_4NO_3 + CaCO_3 \leftrightarrows CaO + CO_2(g) + 2NO_2(g) + N_2(g) + 2H_2O(g) + 2H_2(g)$ (17)

$2NH_4NO_3 + CaCO_3 \leftrightarrows Ca(NO_3)_2 + CO_2(g) + N_2(g) + 3H_2(g) + H_2O(g)$ (18)
$2NH_4NO_3 + CaCO_3 \leftrightarrows Ca(NO_3)_2 + CO_2(g) + N_2O(g) + 4H_2(g)$ (19)
$2NH_4NO_3 + CaCO_3 \leftrightarrows Ca(OH)_2 + CO_2(g) + N_2O(g) + N_2(g) + 3H_2O(g) + 0.5O_2(g)$ (20)
$2NH_4NO_3 + CaCO_3 \leftrightarrows Ca(OH)_2 + CO_2(g) + 2N_2O(g) + 3H_2O(g)$ (21)
$2NH_4NO_3 + CaCO_3 \leftrightarrows CaO_2 + CO_2(g) + 2N_2O(g) + H_2(g) + 3H_2O(g)$ (22)
$2NH_4NO_3 + CaCO_3 \leftrightarrows CaO_2 + CO_2(g) + N_2O(g) + N_2(g) + 4H_2O(g)$ (23)
$2NH_4NO_3 + CaCO_3 \leftrightarrows CaO + CO_2(g) + N_2O(g) + N_2(g) + 4H_2O(g) + 0.5O_2(g)$ (24)
$2NH_4NO_3 + CaCO_3 \leftrightarrows CaO + CO_2(g) + 2N_2O(g) + 4H_2O(g)$ (25)

$2NH_4NO_3 + CaCO_3 + 0.5CuSO_4 \leftrightarrows Ca(NO_3)_2 + CO_2(g) + 1.5NO(g) + 0.25N_2(g) + 0.5CuO + 0.5SO_2(g) + 4H_2(g)$ (26)
$2NH_4NO_3 + CaCO_3 + 0.5CuSO_4 \leftrightarrows Ca(OH)_2 + CO_2(g) + 4NO(g) + 0.5CuO + 0.5SO_2(g) + 1.5H_2O(g) + 1.5H_2(g)$ (27)
$2NH_4NO_3 + CaCO_3 + 0.5CuSO_4 \leftrightarrows CaO_2 + CO_2(g) + 4NO(g) + 0.5CuO + 0.5SO_2(g) + 1.5H_2O(g) + 2.5H_2(g)$ (28)
$2NH_4NO_3 + CaCO_3 + 0.5CuSO_4 \leftrightarrows CaO + CO_2(g) + 4NO(g) + 0.5CuO + 0.5SO_2(g) + 2.5H_2O(g) + 1.5H_2(g)$ (29)

$2NH_4NO_3 + CaCO_3 + 0.5CuSO_4 \leftrightarrows Ca(NO_3)_2 + CO_2(g) + 0.75NO_2(g) + 0.625N_2(g) + 0.5CuO + 0.5SO_2(g) + 4H_2(g)$ (30)
$2NH_4NO_3 + CaCO_3 + 0.5CuSO_4 \leftrightarrows Ca(OH)_2 + CO_2(g) + 2.75NO_2(g) + 0.625N_2(g) + 0.5CuO + 0.5SO_2(g) + 3H_2(g)$ (31)
$2NH_4NO_3 + CaCO_3 + 0.5CuSO_4 \leftrightarrows CaO_2 + CO_2(g) + 2.75NO_2(g) + 062.5N_2(g) + 0.5SO_2(g) + 0.5CuO + 4H_2(g)$ (32)
$2NH_4NO_3 + CaCO_3 + 0.5CuSO_4 \leftrightarrows CaO + CO_2(g) + 3.25NO_2(g) + 0.375N_2(g) + 0.5SO_2(g) + 0.5CuO + 4H_2(g)$ (33)

$2NH_4NO_3 + CaCO_3 + 0.5CuSO_4 \leftrightarrows Ca(NO_3)_2 + CO_2(g) + N_2O(g) + 0.5SO_2(g) + 0.5CuO + 3.5H_2(g) + 0.5H_2O(g)$ (34)
$2NH_4NO_3 + CaCO_3 + 0.5CuSO_4 \leftrightarrows Ca(OH)_2 + CO_2(g) + 2N_2O(g) + 0.5CuO + 0.5SO_2(g) + 3H_2O(g) + 0.25O_2(g)$ (35)
$2NH_4NO_3 + CaCO_3 + 0.5CuSO_4 \leftrightarrows CaO_2 + CO_2(g) + 2N_2O(g) + 0.5CuO + 0.5SO_2(g) + 3.5H_2O(g) + 0.5H_2(g)$ (36)
$2NH_4NO_3 + CaCO_3 + 0.5CuSO_4 \leftrightarrows CaO + CO_2(g) + 2N_2O(g) + 0.5CuO + 0.5SO_2(g) + 4H_2O(g) + 0.25O_2(g)$ (37)

$2NH_4NO_3 + CaCO_3 + 0.5H_3BO_3 \leftrightarrows Ca(NO_3)_2 + CO_2(g) + 2NO(g) + 0.5HBO(g) + 4.5H_2(g)$ (38)
$2NH_4NO_3 + CaCO_3 + 0.5H_3BO_3 \leftrightarrows Ca(OH)_2 + CO_2(g) + 4NO(g) + 0.5HBO(g) + 1.5H_2O(g) + 2H_2(g) + 0.25O_2(g)$ (39)
$2NH_4NO_3 + CaCO_3 + 0.5H_3BO_3 \leftrightarrows Ca(OH)_2 + CO_2(g) + 4NO(g) + 0.5HBO(g) + 2H_2O(g) + 1.5H_2(g)$ (40)
$2NH_4NO_3 + CaCO_3 + 0.5H_3BO_3 \leftrightarrows CaO_2 + CO_2(g) + 4NO(g) + 0.5HBO(g) + 2H_2O(g) + 2.5H_2(g)$ (41)
$2NH_4NO_3 + CaCO_3 + 0.5H_3BO_3 \leftrightarrows CaO + CO_2(g) + 4NO(g) + 0.5HBO(g) + 3H_2O(g) + 1.5H_2(g)$ (42)

Table 1 continued

$2NH_4NO_3 + CaCO_3 + 0.5H_3BO_3 \leftrightarrows Ca(NO_3)_2 + CO_2(g) + NO_2(g) + 0.5N_2(g) + 0.5HBO(g) + 4.5H_2(g)$ (43)
$2NH_4NO_3 + CaCO_3 + 0.5H_3BO_3 \leftrightarrows Ca(OH)_2 + CO_2(g) + 0.5HBO(g) + 3NO_2(g) + 0.5N_2(g) + 3.5H_2(g)$ (44)
$2NH_4NO_3 + CaCO_3 + 0.5H_3BO_3 \leftrightarrows CaO_2 + CO_2(g) + 0.5HBO(g) + 3NO_2(g) + 0.5N_2(g) + 4.5H_2(g)$ (45)
$2NH_4NO_3 + CaCO_3 + 0.5H_3BO_3 \leftrightarrows CaO + CO_2(g) + 0.5HBO(g) + 3.5NO_2(g) + 0.25N_2(g) + 3.5H_2(g)$ (46)

$2NH_4NO_3 + CaCO_3 + 0.5H_3BO_3 \leftrightarrows Ca(NO_3)_2 + CO_2(g) + N_2O(g) + 0.5HBO(g) + 3.5H_2(g) + H_2O(g)$ (47)
$2NH_4NO_3 + CaCO_3 + 0.5H_3BO_3 \leftrightarrows Ca(OH)_2 + CO_2(g) + 0.5HBO(g) + 2N_2O(g) + 3.5H_2O(g) + 0.25O_2(g)$ (48)
$2NH_4NO_3 + CaCO_3 + 0.5H_3BO_3 \leftrightarrows CaO_2 + CO_2(g) + 0.5HBO(g) + 2N_2O(g) + 0.5H_2(g) + 4H_2O(g)$ (49)
$2NH_4NO_3 + CaCO_3 + 0.5H_3BO_3 \leftrightarrows CaO + CO_2(g) + 0.5HBO(g) + 2N_2O(g) + 4.5H_2O(g) + 0.25O_2(g)$ (50)
$2NH_4NO_3 + CaCO_3 + 0.5MnO_2 \leftrightarrows Ca(NO_3)_2 + CO_2(g) + 1.5NO(g) + 0.25N_2(g) + 0.5MnO + 4H_2(g)$ (51)
$2NH_4NO_3 + CaCO_3 + 0.5MnO_2 \leftrightarrows Ca(OH)_2 + CO_2(g) + 4NO(g) + 0.5MnO + 1.5H_2(g) + 1.5H_2O(g)$ (52)
$2NH_4NO_3 + CaCO_3 + 0.5MnO_2 \leftrightarrows CaO_2 + CO_2(g) + 4NO(g) + 0.5MnO + 2.5H_2(g) + 1.5H_2O(g)$ (53)
$2NH_4NO_3 + CaCO_3 + 0.5MnO_2 \leftrightarrows CaO + CO_2(g) + 4NO(g) + 0.5MnO + 1.5H_2(g) + 2.5H_2O(g)$ (54)

$2NH_4NO_3 + CaCO_3 + 0.5MnO_2 \leftrightarrows Ca(NO_3)_2 + CO_2(g) + 0.75NO_2(g) + 0.625N_2(g) + 0.5MnO(g) + 4H_2(g)$ (55)
$2NH_4NO_3 + CaCO_3 + 0.5MnO_2 \leftrightarrows Ca(OH)_2 + CO_2(g) + 0.5MnO + 2.75NO_2(g) + 0.625N_2(g) + 3H_2(g)$ (56)
$2NH_4NO_3 + CaCO_3 + 0.5MnO_2 \leftrightarrows CaO_2 + CO_2(g) + 0.5MnO + 2.75NO_2(g) + 0.625N_2(g) + 4H_2(g)$ (57)
$2NH_4NO_3 + CaCO_3 + 0.5MnO_2 \leftrightarrows CaO + CO_2(g) + 3.25NO_2(g) + 0.375N_2(g) + 0.5MnO + 4H_2(g)$ (58)
$2NH_4NO_3 + CaCO_3 + 0.5MnO_2 \leftrightarrows Ca(NO_3)_2 + CO_2(g) + N_2O(g) + 0.5MnO + 3.5H_2(g) + 0.5H_2O(g)$ (59)
$2NH_4NO_3 + CaCO_3 + 0.5MnO_2 \leftrightarrows Ca(OH)_2 + CO_2(g) + 2N_2O(g) + 0.5MnO + 0.25O_2(g) + 3H_2O(g)$ (60)
$2NH_4NO_3 + CaCO_3 + 0.5MnO_2 \leftrightarrows CaO_2 + CO_2(g) + 2N_2O(g) + 0.5MnO + 0.5H_2(g) + 3.5H_2O(g)$ (61)
$2NH_4NO_3 + CaCO_3 + 0.5MnO_2 \leftrightarrows CaO + CO_2(g) + 2N_2O(g) + 0.5MnO + 0.25O_2(g) + 4H_2O(g)$ (62)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 \leftrightarrows 0.5Ca(NO_3)_2 + 0.5\ Mg(NO_3)_2 + CO_2(g) + NO(g) + 0.5N_2(g) + 4H_2(g)$ (63)
$2NH_4NO_3 + 0.5CaMg(CO_3)_2 \leftrightarrows 0.5Ca(OH)_2 + 0.5\ Mg(OH)_2 + CO_2(g) + 4NO(g) + 2H_2(g) + H_2O(g)$ (64)
$2NH_4NO_3 + 0.5CaMg(CO_3)_2 \leftrightarrows 0.5CaO_2 + 0.5\ MgO_2 + CO_2(g) + 4NO(g) + 3H_2(g) + H_2O(g)$ (65)
$2NH_4NO_3 + 0.5CaMg(CO_3)_2 \leftrightarrows 0.5CaO + 0.5\ MgO + CO_2(g) + 4NO(g) + 2H_2(g) + 2H_2O(g)$ (66)
$2NH_4NO_3 + 0.5CaMg(CO_3)_2 \leftrightarrows 0.5Ca(NO_3)_2 + 0.5\ Mg(NO_3)_2 + CO_2(g) + N_2(g) + H_2O(g) + 3H_2(g)$ (67)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5CuSO_4 \leftrightarrows$
$0.5Ca(NO_3)_2 + 0.5\ Mg(NO_3)_2 + CO_2(g) + 1.5NO(g) + 0.5CuO + 0.5SO_2(g) + 0.25N_2(g) + 4H_2(g)$ (68)
$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5CuSO_4 \leftrightarrows$
$0.5Ca(OH)_2 + 0.5\ Mg(OH)_2 + CO_2(g) + 4NO(g) + 0.5CuO + 0.5SO_2(g) + 1.5H_2O(g) + 1.5H_2(g)$ (69)
$2NH_4NO_3 + 0.5CaMg(CO3)_2 + 0.5CuSO_4 \leftrightarrows$
$0.5CaO_2 + 0.5\ MgO_2 + CO_2(g) + 4NO(g) + 0.5CuO + 0.5SO_2(g) + 1.5H_2O(g) + 2.5H_2(g)$ (70)
$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5CuSO_4 \leftrightarrows$
$0.5CaO + 0.5\ MgO + CO_2(g) + 4NO(g) + 0.5CuO + 0.5SO_2(g) + 2.5H_2O(g) + 1.5H_2(g)$ (71)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5H_3BO_3 \leftrightarrows 0.5Ca(NO_3)_2 + 0.5\ Mg(NO_3)_2 + CO_2(g) + 2NO(g) + 0.5HBO(g) + 4.5H_2(g)$ (72)
$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5H_3BO_3 \leftrightarrows$
$0.5Ca(OH)_2 + 0.5\ Mg(OH)_2 + CO_2(g) + 4NO(g) + 0.5HBO(g) + 2H_2O(g) + 1.5H_2(g)$ (73)
$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5H_3BO_3 \leftrightarrows 0.5CaO_2 + 0.5\ MgO_2 + CO_2(g) + 4NO(g) + 0.5HBO(g) + 2H_2O(g) + 2.5H_2(g)$ (74)
$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5H_3BO_3 \leftrightarrows 0.5CaO + 0.5MgO + CO_2(g) + 4NO(g) + 0.5HBO(g) + 3H_2O(g) + 1.5H_2(g)$ (75)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5MnO_2 \leftrightarrows 0.5Ca(NO_3)_2 + 0.5Mg(NO_3)_2 + CO_2(g) + 1.5NO(g) + 0.25N_2(g) + 0.5MnO + 4H_2(g)$ (76)
$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5MnO_2 \leftrightarrows 0.5Ca(OH)_2 + 0.5\ Mg(OH)_2 + CO_2(g) + 4NO(g) + 0.5MnO + 1.5H_2(g) + 1.5H_2O(g)$ (77)
$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5MnO_2 \leftrightarrows 0.5CaO_2 + 0.5\ MgO_2 + CO_2(g) + 4NO(g) + 0.5MnO + 2.5H_2(g) + 1.5H_2O(g)$ (78)
$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5MnO_2 \leftrightarrows 0.5CaO + 0.5\ MgO + CO_2(g) + 4NO(g) + 0.5MnO + 1.5H_2(g) + 2.5H_2O(g)$ (79)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 \leftrightarrows 0.5Ca(NO_3)_2 + 0.5Mg(NO_3)_2 + CO_2(g) + 0.5NO_2(g) + 0.75N_2(g) + 4H_2(g)$ (80)
$2NH_4NO_3 + 0.5CaMg(CO_3)_2 \leftrightarrows 0.5Ca(NO_3)_2 + 0.5\ Mg(NO_3)_2 + CO_2(g) + N_2(g) + H_2O(g) + 3H_2(g)$ (81)
$2NH_4NO_3 + 0.5CaMg(CO_3)_2 \leftrightarrows 0.5Ca(OH)_2 + 0.5\ Mg(OH)_2 + CO_2(g) + 2NO_2(g) + N_2(g) + H_2O(g) + 2H_2(g)$ (82)
$2NH_4NO_3 + 0.5CaMg(CO_3)_2 \leftrightarrows 0.5CaO_2 + 0.5MgO_2 + CO_2(g) + 2NO_2(g) + N_2(g) + H_2O(g) + 3H_2(g)$ (83)
$2NH_4NO_3 + 0.5CaMg(CO_3)_2 \leftrightarrows 0.5CaO + 0.5MgO + CO_2(g) + 2NO_2(g) + N_2(g) + 2H_2O(g) + 2H_2(g)$ (84)

Table 1 continued

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5CuSO_4 \leftrightarrows 0.5Ca(NO_3)_2 + 0.5Ca(NO_3)_2 + CO_2(g) + 0.75NO_2(g) + 0.625N_2(g) + 0.5CuO + 0.5SO_2(g) + 4H_2(g)$ (85)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5CuSO_4 \leftrightarrows 0.5Ca(OH)_2 + 0.5\ Mg(OH)_2 + CO_2(g) + 2.75NO_2(g) + 0.625N_2(g) + 0.5CuO + 0.5SO_2(g) + 3H_2(g)$ (86)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5CuSO_4 \leftrightarrows 0.5CaO_2 + 0.5MgO_2 + CO_2(g) + 2.75NO_2(g) + 0.625N_2(g) + 0.5SO_2(g) + 0.5CuO + 4H_2(g)$ (87)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5CuSO_4 \leftrightarrows 0.5CaO + 0.5MgO + CO_2(g) + 3.25NO_2(g) + 0.375N_2(g) + 0.5SO_2(g) + 0.5CuO + 4H_2(g)$ (88)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5H_3BO_3 \leftrightarrows 0.5Ca(NO_3)_2 + 0.5Ca(NO_3)_2 + CO_2(g) + NO_2(g) + 0.5N_2(g) + 0.5HBO(g) + 4.5H_2(g)$ (89)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5H_3BO_3 \leftrightarrows 0.5Ca(OH)_2 + 0.5\ Mg(OH)_2 + CO_2(g) + 0.5HBO(g) + 3NO_2(g) + 0.5N_2(g) + 3.5H_2(g)$ (90)

$2NH_4NO_3 + 0.5\ Mg(CaCO_3)_2 + 0.5H_3BO_3 \leftrightarrows 0.5CaO_2 + 0.5MgO_2 + CO_2(g) + 0.5HBO(g) + 3NO_2(g) + 0.5N_2(g) + 4.5H_2(g)$ (91)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5H_3BO_3 \leftrightarrows 0.5CaO + 0.5MgO + CO_2(g) + 0.5HBO(g) + 3.5NO_2(g) + 0.25N_2(g) + 4.5H_2(g)$ (92)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5MnO_2 \leftrightarrows 0.5Ca(NO_3)_2 + 0.5Ca(NO_3)_2 + CO_2(g) + 0.75NO_2(g) + 0.625N_2(g) + 0.5MnO + 4H_2(g)$ (93)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5MnO_2 \leftrightarrows 0.5Ca(OH)_2 + 0.5\ Mg(OH)_2 + CO_2(g) + 0.5MnO + 2.75NO_2(g) + 0.625N_2(g) + 3H_2(g)$ (94)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5MnO_2 \leftrightarrows 0.5CaO_2 + 0.5MgO_2 + CO_2(g) + 0.5MnO + 2.75NO_2(g) + 0.625N_2(g) + 4H_2(g)$ (95)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5MnO_2 \leftrightarrows 0.5CaO + 0.5MgO + CO_2(g) + 3.25NO_2(g) + 0.375N_2(g) + 0.5MnO + 4H_2(g)$ (96)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 \leftrightarrows 0.5Ca(NO_3)_2 + 0.5\ Mg(NO_3)_2 + CO_2(g) + N_2(g) + 3H_2(g) + H_2O(g)$ (97)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 \leftrightarrows 0.5Ca(NO_3)_2 + 0.5\ Mg(NO_3)_2 + CO_2(g) + N_2O(g) + 4H_2(g)$ (98)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 \leftrightarrows 0.5Ca(OH)_2 + 0.5\ Mg(OH)_2 + CO_2(g) + 2N_2O(g) + 3H_2O(g)$ (99)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 \leftrightarrows 0.5Ca(OH)_2 + 0.5\ Mg(OH)_2 + CO_2(g) + N_2O(g) + N_2(g) + 3H_2O(g) + 0.5O_2(g)$ (100)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 \leftrightarrows 0.5CaO_2 + 0.5\ MgO_2 + CO_2(g) + 2N_2O(g) + H_2(g) + 3H_2O(g)$ (101)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 \leftrightarrows 0.5CaO_2 + 0.5\ MgO_2 + CO_2(g) + N_2O(g) + N_2(g) + 4H_2O(g)$ (102)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 \leftrightarrows 0.5CaO + 0.5\ MgO + CO_2(g) + N_2O(g) + N_2(g) + 4H_2O(g) + 0.5O_2(g)$ (103)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 \leftrightarrows 0.5CaO + 0.5\ MgO + CO_2(g) + 2N_2O(g) + 4H_2O(g)$ (104)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5CuSO_4 \leftrightarrows 0.5Ca(NO_3)_2 + 0.5Ca(NO_3)_2 + CO_2(g) + N_2O(g) + 0.5SO_2(g) + 0.5CuO + 3.5H_2(g) + 0.5H_2O(g)$ (105)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5CuSO_4 \leftrightarrows 0.5Ca(OH)_2 + 0.5\ Mg(OH)_2 + CO_2(g) + 2N_2O(g) + 0.5CuO + 0.5SO_2(g) + 3H_2O(g) + 0.25O_2(g)$ (106)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5CuSO_4 \leftrightarrows 0.5CaO_2 + 0.5\ MgO_2 + CO_2(g) + 2N_2O(g) + 0.5CuO + 0.5SO_2(g) + 3.5H_2O(g) + 0.5H_2(g)$ (107)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5CuSO_4 \leftrightarrows 0.5CaO + 0.5MgO + CO_2(g) + 2N_2O(g) + 0.5CuO + 0.5SO_2(g) + 4H_2O(g) + 0.25O_2(g)$ (108)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5H_3BO_3 \leftrightarrows 0.5Ca(NO_3)_2 + 0.5Ca(NO_3)_2 + CO_2(g) + N_2O(g) + 0.5HBO(g) + 3.5H_2(g) + H_2O(g)$ (109)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5H_3BO_3 \leftrightarrows 0.5Ca(OH)_2 + 0.5Mg(OH)_2 + CO_2(g) + 0.5HBO(g) + 2N_2O(g) + 3.5H_2O(g) + 0.25O_2(g)$ (110)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5H_3BO_3 \leftrightarrows CaO_2 + MgO_2 + CO_2(g) + 0.5HBO(g) + 2N_2O(g) + 0.5H_2(g) + 4H_2O(g)$ (111)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5H_3BO_3 \leftrightarrows 0.5CaO + 0.5MgO + CO_2(g) + 0.5HBO(g) + 2N_2O(g) + 4.5H_2O(g) + 0.025O_2(g)$ (112)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5MnO_2 \leftrightarrows 0.5Ca(NO_3)_2 + 0.5Ca(NO_3)_2 + CO_2(g) + N_2O(g) + 0.5MnO + 3.5H_2(g) + 0.5H_2O(g)$ (113)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5MnO_2 \leftrightarrows 0.5Ca(OH)_2 + 0.5Mg(OH)_2 + CO_2(g) + 2N_2O(g) + 0.5MnO + 0.25O_2(g) + 3H_2O(g)$ (114)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5MnO_2 \leftrightarrows 0.5CaO_2 + 0.5MgO_2 + CO_2(g) + 2N_2O(g) + 0.5MnO + 0.5H_2(g) + 3.5H_2O(g)$ (115)

$2NH_4NO_3 + 0.5CaMg(CO_3)_2 + 0.5MnO_2 \leftrightarrows 0.5CaO + 0.5MgO + CO_2(g) + 2N_2O(g) + 0.5MnO + 0.25O_2(g) + 4H_2O(g)$ (116)

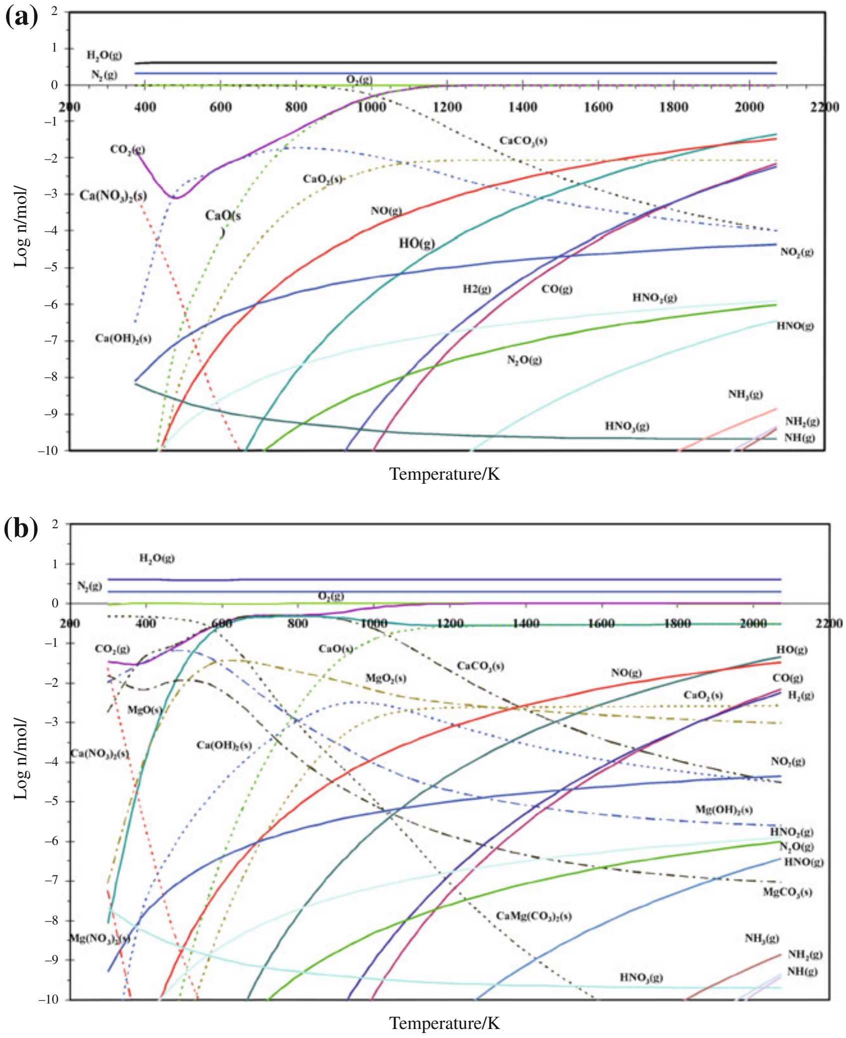


Fig. 1 Temperature dependencies of equilibrium amounts of compounds (log n, mol) in the system $2NH_4NO_3$–$CaCO_3$ (**a**) and $2NH_4NO_3$–$0.5CaMg(CO_3)_2$ (**b**)

873 and 1473 K the SO_2(g) and SO_3(g) content is 10^{-6}–10^{-9} mol and the content is SO(g) 10^{-15}–10^{-16} mol with carbonates. Without carbonates these amounts are 10^{-2}–10^{-4} mol and 10^{-10} mol, respectively. At temperatures above 1473 K the content of SO_2(g) and SO_3(g) is 10^{-2}–10^{-5} mol and of SO(g) 10^{-6}–10^{-7} mol in both systems—with and without carbonates (Table 3, Fig. 2).

It can be seen that in the system of AN with $CuSO_4$(s), at the mole ratio of AN/$CuSO_4$, 1/0.01 or 1/0.05 the content of $CuSO_4$(s) began to decrease at 700–800 K being at 1273 K on the levels of 1.26×10^{-7} and 3.16×10^{-6}, and at 1773 K 6.76×10^{-12} and 1.70×10^{-10} mol, respectively. One intermediate Cu-containing compound is $Cu(OH)_2$(s), but its maximum content at 873–973 K does not exceed 10^{-6} mol. The content of CuO(s) at 973–1073 K reaches 10^{-2} mol and the same level of Cu_2O(s) can be seen at 1273–1373 K (Fig. 2a).

In the system of AN and carbonates with $CuSO_4$(s), the $Cu(OH)_2$(s) content decreases from 10^{-3} mol at 473 K to 10^{-7} mol at temperatures higher than 1073–1373 K. The content of CuO(s) is 10^{-3}–10^{-2} mol in the broad temperature interval studied–from 373 K up to 2073 K. The content of Cu_2O(s) reaches 10^{-5} mol at 873–1073 K and 10^{-3}–10^{-2} mol at 1573 K. The content of $CaSO_4$(s) is constant–10^{-2} mol up to 1400–1500 K and decreases to 10^{-4} mol at 2073 K. The amount of $MgSO_4$(s) varies in between 10^{-3}–10^{-2} mol along the temperature range from 373 to 2073 K. The $CaSO_3$(s) and $MgSO_3$(s) content reaches the maximum of 10^{-5} and 10^{-12} mol, respectively, at 1773 K and 1573 K. (Fig. 2b, c).

H_3BO_3

Comparing the systems with H_3BO_3(s) additive based on AN with carbonates or without carbonates, the content of NO(g) remains practically on the same level at any temperature in all the systems studied. The NO_2(g) and N_2O(g) content at lower temperatures is also on the same

Table 2 Equilibrium concentrations of NO, NO_2 and N_2O at different temperatures

System	Amount of compound/mol		
Temperature/K	NO	NO_2	N_2O
NH_4NO_3 (AN)			
773	5.01×10^{-6}	1.75×10^{-6}	2.70×10^{-10}
1273	1.26×10^{-3}	1.31×10^{-5}	4.43×10^{-8}
1773	1.38×10^{-2}	3.32×10^{-5}	4.39×10^{-7}
2AN + $CaCO_3$			
773	5.01×10^{-6}	1.74×10^{-6}	2.70×10^{-10}
1273	1.24×10^{-3}	1.22×10^{-5}	4.16×10^{-8}
1773	1.38×10^{-2}	3.14×10^{-5}	4.09×10^{-7}
2AN + $MgCO_3$			
773	4.94×10^{-6}	1.60×10^{-6}	2.51×10^{-10}
1273	1.24×10^{-3}	1.22×10^{-5}	4.14×10^{-8}
1773	1.38×10^{-2}	3.12×10^{-5}	4.10×10^{-7}
2AN + $0.5CaMg(CO_3)_2$			
773	4.97×10^{-6}	1.67×10^{-6}	2.61×10^{-10}
1273	1.24×10^{-3}	1.22×10^{-5}	4.16×10^{-8}
1773	1.38×10^{-2}	3.14×10^{-5}	4.10×10^{-7}
2AN + CaO			
773	5.01×10^{-6}	1.80×10^{-6}	2.79×10^{-10}
1273	1.24×10^{-3}	1.30×10^{-5}	4.42×10^{-8}
1773	1.38×10^{-2}	3.31×10^{-5}	4.37×10^{-7}
2AN + MgO			
773	4.93×10^{-6}	1.70×10^{-6}	2.70×10^{-10}
1273	1.24×10^{-3}	1.30×10^{-5}	4.43×10^{-8}
1773	1.38×10^{-2}	3.32×10^{-5}	4.39×10^{-7}

level, but when increasing the temperature, the increase in the content of both gases is about 7–8%, like it is in the case of $CuSO_4$(s) additive (Table 3).

The most probable gaseous compound of boron formed in these systems is HBO(g) whose content seems to be on the level of the added amount of H_3BO_3(s) –1 × 10^{-2} or 5 × 10^{-2} mol. The content of the other gaseous boron compounds, like H_3BO_2, HBO_2, BO_2, BO is 10^{-35}–10^{-11} mol and their content is increasing with temperature (Table 3).

MnO_2

No differences in the content of N-containing gaseous compounds were found, when comparing AN–carbonates systems with and without MnO_2(s) additive, as well as when comparing with these based on pure AN with MnO_2(s) (Tables 2 and 3).

The content of MnO_2(s), MnO(s) and $Mn(OH)_2$(s) was 3–15 times higher (Table 3) and that of Mn_3O_4(s) and Mn_2O_3(s) 10^3–10^1 times lower in the systems with carbonates as compared to the systems without carbonates.

Probable reactions

Considering the data from equilibrium calculations and that thermodynamically the most probable (present in the highest amounts) Ca, Mg-containing compounds were CaO(s), MgO(s), CaO_2(s), MgO_2(s), $Ca(OH)_2$(s), $Mg(OH)_2$(s), $Ca(NO_3)_2$(s) and $Mg(NO_3)_2$(s) and N-containing compounds NO(g), NO_2(g) and N_2O(g), the temperature dependencies of Gibbs free energy changes ΔG_T were calculated for reactions (R) 1–116 in the temperature range of 273–2073 K to estimate the most probable reactions in the systems studied (Table 1). The calculations were based on the initial amount of two moles of AN.

System 2AN–$CaCO_3$/$0.5CaMg(CO_3)_2$

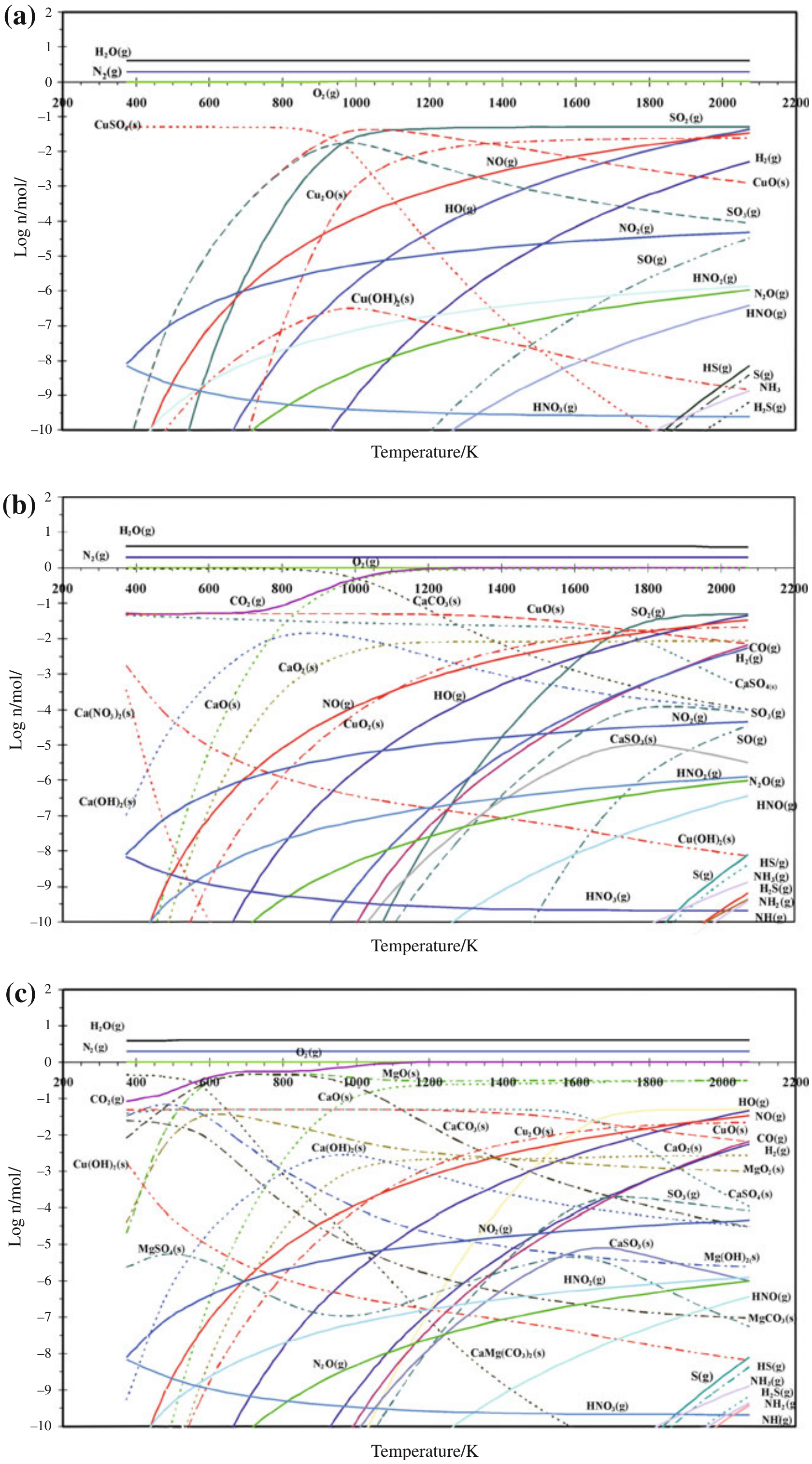
Reactions in the 2AN–$CaCO_3$ system with the simultaneous formation of NO(g) and N_2(g) are more probable than those where only NO(g) is formed. The NO_2(g) or N_2O(g) formation becomes more probable at a higher content of the simultaneously formed N_2(g) in the system. Most of these reactions are already probable at room temperature or over 373–473 K (Fig. 3). For example, if simultaneous formation of NO(g) and N_2(g) is assumed (R 5, 7, 9), the formation of $Ca(OH)_2$(s), CaO(s) and CaO_2(s) is already probable at room temperature, but if only the formation of NO(g) is assumed (R 4, 6, 8), the $Ca(OH)_2$(s) and CaO(s) formation becomes probable at temperatures over 600–620 K and CaO_2(s) over 850 K. The formation of $Ca(NO_3)_2$(s) together with NO(g) and N_2(g) (R 3) is probable at temperatures over 1000 K, but with N_2(g) alone (R 2), over 473 K (Fig. 3a).

The formation of 2 mol of NO_2(g) with 1 mol of N_2(g) (R 13, 15, 17) instead of 2.5 or 3 mol of NO_2(g) with 0.75 or 1 mol of N_2(g) (R 12, 14, 16) shifts the temperature of possible formation of $Ca(OH)_2$(s) and CaO(s) from 370–420 K to 680 and 980 K, respectively, and of CaO_2(s) formation from 680 to 980 K. The formation of $Ca(NO_3)_2$(s) with NO(g) and N_2(g) as reaction products becomes probable at $T > 973$ K, and with N_2(g) alone, at $T > 473$ K (Fig. 3b).

The formation of N_2O(g) (with or without N_2(g)) and solid phases like $Ca(OH)_2$, CaO and CaO_2 is already probable at room temperature and is definitely more probable than the explosive decomposition of AN. The formation of $Ca(NO_3)_2$(s) with N_2O(g) becomes probable at $T > 1170$ K and with N_2(g) over 470 K (Fig. 3c).

In the system 2AN–$0.5CaMg(CO_3)_2$ with NO(g) as the gaseous product, the formation of $Ca(OH)_2$(s) and $Mg(OH)_2$(s) (R 64) becomes probable at $T > 590$ K; CaO(s) and MgO(s) (R 66) at $T > 600$ K, and CaO_2(s) and MgO_2(s) (R 65) at $T > 810$ K i.e. at 20–40 K lower temperatures than in the case of the respective reactions in the

Fig. 2 Temperature dependencies of equilibrium amounts of compounds (log n, mol) in the system $2NH_4NO_3$–$0.05CuSO_4$ (**a**), $2NH_4NO_3$–$CaCO_3$–$0.05CuSO_4$ (**b**) and $2NH_4NO_3$–$0.5CaMg(CO_3)_2$–$0.05CuSO_4$ (**c**)



system 2AN–$CaCO_3$. Thereby, the formation of $Ca(NO_3)_2$(s), $Mg(NO_3)_2$(s) and NO(g) with the simultaneous formation of N_2(g) (R63) becomes probable at $T > 1050$ K or if only N_2(g) (and no NO(g)) is formed (R 64), at $T > 530$ K, i.e. at 50–60 K higher temperatures than in the case of the system 2AN–$CaCO_3$ (Fig. 4).

The formation of NO_2(g) and N_2(g) as N-containing gaseous compounds with $Ca(OH)_2$(s) and $Mg(OH)_2$(s) (R 82) is probable at temperatures over 373 K, with CaO_2(s) and MgO_2(s) (R 83) over 640 K, and with CaO(s) and MgO(s) (R 84) over 400 K i.e. at 20–50 K lower temperatures than in the system 2AN–$CaCO_3$. Reactions with $Ca(NO_3)_2$(s),

Table 3 Equilibrium concentrations of different compounds at different temperatures

System	Amount of compound/mol					
Temperature/K	NO	NO_2	N_2O	SO	SO_2	SO_3
$2AN + 0.01CuSO_4$						
773	5.01×10^{-6}	1.75×10^{-6}	2.70×10^{-10}	3.16×10^{-21}	3.24×10^{-5}	7.08×10^{-4}
1273	1.26×10^{-3}	1.31×10^{-5}	4.43×10^{-8}	1.02×10^{-10}	9.55×10^{-3}	5.24×10^{-4}
1773	1.38×10^{-2}	3.32×10^{-5}	4.39×10^{-7}	3.39×10^{-7}	1.10×10^{-3}	4.37×10^{-5}
$2AN + 0.05CuSO_4$						
773	5.01×10^{-6}	1.75×10^{-6}	2.70×10^{-10}	7.24×10^{-21}	7.40×10^{-5}	1.62×10^{-3}
1273	1.26×10^{-3}	1.31×10^{-5}	4.43×10^{-8}	5.13×10^{-10}	4.79×10^{-2}	2.69×10^{-3}
1773	1.38×10^{-2}	3.32×10^{-5}	4.39×10^{-7}	1.70×10^{-6}	5.01×10^{-2}	2.19×10^{-4}
$2AN + CaCO_3 + 0.01CuSO_4$						
773	5.01×10^{-6}	1.75×10^{-6}	2.70×10^{-10}	3.23×10^{-35}	3.31×10^{-19}	7.08×10^{-18}
1273	1.26×10^{-3}	1.22×10^{-5}	4.17×10^{-8}	6.76×10^{-16}	5.82×10^{-8}	3.09×10^{-9}
1773	1.38×10^{-2}	3.16×10^{-5}	4.10×10^{-7}	1.86×10^{-7}	5.01×10^{-3}	2.04×10^{-5}
$2AN + CaCO_3 + 0.05CuSO_4$						
773	5.01×10^{-6}	1.75×10^{-6}	2.70×10^{-10}	2.63×10^{-34}	2.69×10^{-18}	5.89×10^{-17}
1273	1.26×10^{-3}	1.23×10^{-5}	4.17×10^{-8}	3.55×10^{-15}	3.09×10^{-7}	1.58×10^{-8}
1773	1.38×10^{-2}	3.16×10^{-5}	4.12×10^{-7}	9.20×10^{-7}	2.51×10^{-2}	1.04×10^{-4}
$2AN + 0.5CaMg(CO_3)_2 + 0.01CuSO_4$						
773	5.01×10^{-6}	1.66×10^{-6}	2.70×10^{-10}	3.23×10^{-35}	6.92×10^{-17}	1.45×10^{-15}
1273	1.26×10^{-3}	1.22×10^{-5}	4.17×10^{-8}	6.76×10^{-16}	2.34×10^{-6}	1.20×10^{-7}
1773	1.38×10^{-2}	3.16×10^{-5}	4.10×10^{-7}	1.86×10^{-7}	4.47×10^{-2}	1.86×10^{-4}
$2AN + 0.5CaMg(CO_3)_2 + 0.05CuSO_4$						
773	5.01×10^{-6}	1.70×10^{-6}	2.70×10^{-10}	2.63×10^{-34}	6.93×10^{-17}	1.44×10^{-15}
1273	1.26×10^{-3}	1.23×10^{-5}	4.17×10^{-8}	3.55×10^{-15}	2.32×10^{-6}	1.20×10^{-7}
1773	1.38×10^{-2}	3.16×10^{-5}	4.12×10^{-7}	9.20×10^{-7}	4.47×10^{-2}	1.86×10^{-4}
Temperature/K	NO	NO_2	N_2O	HBO	HBO_2	BO_2
$2AN + 0.01H_3BO_3$						
773	5.01×10^{-6}	1.73×10^{-6}	2.69×10^{-10}	1×10^{-2}	7.41×10^{-25}	7.50×10^{-31}
1273	1.26×10^{-3}	1.32×10^{-5}	4.47×10^{-8}	1×10^{-2}	8.51×10^{-18}	1.32×10^{-20}
1773	1.38×10^{-2}	3.32×10^{-5}	4.37×10^{-7}	1×10^{-2}	9.77×10^{-15}	3.98×10^{-16}
$2AN + 0.05\ H_3BO_3$						
773	5.01×10^{-6}	1.73×10^{-6}	2.69×10^{-10}	5×10^{-2}	3.72×10^{-24}	3.80×10^{-30}
1273	1.26×10^{-3}	1.32×10^{-5}	4.47×10^{-8}	5×10^{-2}	3.98×10^{-17}	6.61×10^{-20}
1773	1.38×10^{-2}	3.32×10^{-5}	4.37×10^{-7}	5×10^{-2}	5.01×10^{-14}	2.00×10^{-15}
$2AN + CaCO_3 + 0.01\ H_3BO_3$						
773	5.01×10^{-6}	1.74×10^{-6}	2.69×10^{-10}	1×10^{-2}	7.41×10^{-25}	7.58×10^{-31}
1273	1.25×10^{-3}	1.22×10^{-5}	4.16×10^{-8}	1×10^{-2}	7.94×10^{-18}	1.28×10^{-20}
1773	1.38×10^{-2}	3.16×10^{-5}	4.09×10^{-7}	1×10^{-2}	9.33×10^{-15}	3.89×10^{-16}
$2AN + CaCO_3 + 0.05\ H_3BO_3$						
773	5.01×10^{-6}	1.73×10^{-6}	2.69×10^{-10}	5×10^{-2}	3.71×10^{-24}	3.80×10^{-30}
1273	1.26×10^{-3}	1.26×10^{-5}	4.17×10^{-8}	5×10^{-2}	3.98×10^{-17}	6.46×10^{-20}
1773	1.38×10^{-2}	3.16×10^{-5}	4.11×10^{-7}	5×10^{-2}	4.68×10^{-14}	1.90×10^{-15}
$2AN + 0.5CaMg(CO_3)_2 + 0.01\ H_3BO_3$						
773	5.01×10^{-6}	1.72×10^{-6}	2.65×10^{-10}	1×10^{-2}	7.24×10^{-25}	7.31×10^{-31}
1273	1.26×10^{-3}	1.23×10^{-5}	4.16×10^{-8}	1×10^{-2}	7.94×10^{-18}	1.29×10^{-20}
1773	1.38×10^{-2}	3.16×10^{-5}	4.10×10^{-7}	1×10^{-2}	9.24×10^{-15}	3.80×10^{-16}

Table 3 continued

Temperature/K	NO	NO_2	N_2O	HBO	HBO_2	BO_2
$2AN + 0.5CaMg(CO_3)_2 + 0.05\ H_3BO_3$						
773	5.01×10^{-6}	1.71×10^{-6}	2.63×10^{-10}	5×10^{-2}	3.63×10^{-24}	3.71×10^{-30}
1273	1.26×10^{-3}	1.24×10^{-5}	4.17×10^{-8}	5×10^{-2}	3.98×10^{-17}	6.46×10^{-20}
1773	1.38×10^{-2}	3.16×10^{-5}	4.12×10^{-7}	5×10^{-2}	4.67×10^{-14}	1.92×10^{-15}
Temperature/K	NO	NO_2	N_2O	MnO	MnO_2	$Mn(OH)_2$
$2AN + 0.01MnO_2$						
773	5.01×10^{-6}	1.73×10^{-6}	2.69×10^{-10}	3.00×10^{-6}	2.92×10^{-3}	3.63×10^{-11}
1273	1.26×10^{-3}	1.32×10^{-5}	4.45×10^{-8}	4.75×10^{-4}	1.41×10^{-4}	2.32×10^{-12}
1773	1.38×10^{-2}	3.32×10^{-5}	4.37×10^{-7}	3.60×10^{-3}	3.36×10^{-5}	1.47×10^{-13}
$2AN + 0.05\ MnO_2$						
773	5.01×10^{-6}	1.73×10^{-6}	2.69×10^{-10}	1.50×10^{-5}	1.47×10^{-2}	1.81×10^{-10}
1273	1.26×10^{-3}	1.31×10^{-5}	4.47×10^{-8}	2.40×10^{-3}	7.07×10^{-4}	1.15×10^{-11}
1773	1.38×10^{-2}	3.32×10^{-5}	4.45×10^{-7}	1.80×10^{-2}	1.69×10^{-4}	7.31×10^{-13}
$2AN + CaCO_3 + 0.01\ MnO_2$						
773	5.01×10^{-6}	1.73×10^{-6}	2.69×10^{-10}	9.86×10^{-6}	9.57×10^{-3}	1.18×10^{-10}
1273	1.25×10^{-3}	1.25×10^{-5}	4.17×10^{-8}	6.08×10^{-3}	1.69×10^{-3}	2.60×10^{-11}
1773	1.38×10^{-2}	3.16×10^{-5}	4.07×10^{-7}	9.86×10^{-3}	8.59×10^{-5}	3.52×10^{-13}
$2AN + CaCO_3 + 0.05\ MnO_2$						
773	5.01×10^{-6}	1.73×10^{-6}	2.69×10^{-10}	4.33×10^{-5}	4.21×10^{-2}	5.18×10^{-10}
1273	1.24×10^{-3}	1.26×10^{-5}	4.16×10^{-8}	1.90×10^{-2}	5.30×10^{-3}	8.12×10^{-11}
1773	1.38×10^{-2}	3.16×10^{-5}	4.16×10^{-7}	4.81×10^{-2}	4.22×10^{-4}	1.71×10^{-12}
$2AN + 0.5CaMg(CO_3)_2 + 0.01\ MnO_2$						
773	5.01×10^{-6}	1.66×10^{-6}	2.63×10^{-10}	1.07×10^{-5}	9.99×10^{-3}	1.20×10^{-10}
1273	1.26×10^{-3}	1.22×10^{-5}	4.17×10^{-8}	7.34×10^{-3}	2.03×10^{-3}	3.13×10^{-11}
1773	1.38×10^{-2}	3.16×10^{-5}	4.07×10^{-7}	9.91×10^{-3}	8.64×10^{-5}	3.54×10^{-13}
$2AN + 0.5CaMg(CO_3)_2 + 0.05\ MnO_2$						
773	5.01×10^{-6}	1.66×10^{-6}	2.57×10^{-10}	5.32×10^{-5}	4.98×10^{-2}	6.00×10^{-10}
1273	1.26×10^{-3}	1.24×10^{-5}	4.16×10^{-8}	2.37×10^{-2}	6.61×10^{-3}	1.01×10^{-10}
1773	1.38×10^{-2}	3.16×10^{-5}	4.16×10^{-7}	4.94×10^{-2}	2.73×10^{-4}	8.09×10^{-13}

$Mg(NO_3)_2$(s) and NO_2(g) + N_2(g) formation (R 80) are probable at $T > 1000$ K, and with only N_2(g) formation (R 81) at $T > 540$ K or at 50 K higher temperature than in the system 2AN–$CaCO_3$.

The formation of N_2O(g) (with or without N_2(g)) along with $Ca(OH)_2$(s) and $Mg(OH)_2$(s), CaO(s) and MgO(s) or CaO_2(s) and MgO_2(s) (R 99–104) is also probable at room temperature like in the system 2AN–$CaCO_3$. $Ca(NO_3)_2$(s) and $Mg(NO_3)_2$(s) formation with N_2O(g) (R98) is probable at temperatures over 1200 K and with N_2(g) (R 97) over 550 K which is by 30 K (R 98) and 80 K (R 97) higher than in 2AN–$CaCO_3$ system.

System 2AN–$CaCO_3$/0.5$CaMg(CO_3)_2$–$CuSO_4$, H_3BO_3 or MnO_2

The influence of $CuSO_4$(s), H_3BO_3(s) and MnO_2(s) additive (initial amount 0.05 mol) in the systems 2AN–$CaCO_3$ and 2AN–0.5$CaMg(CO_3)_2$ on the temperature dependencies of ΔG_T for the reactions between AN(s) and $CaCO_3$(s) or AN(s) and $CaMg(CO_3)_2$(s) with the NO(g), NO_2(g) or N_2O(g) formation as gaseous N-containing compounds and CaO(s), MgO(s); CaO_2(s), MgO_2(s); $Ca(OH)_2$(s), $Mg(OH)_2$(s) and $Ca(NO_3)_2$(s), $Mg(NO_3)_2$(s) as solids was minor (shift by 5–10 K) or was absent at all.

$CuSO_4$(s) additive (0.5 mol) shifted the probability of the formation of NO(g), $Ca(NO_3)_2$(s) and $Mg(NO_3)_2$(s) (R 26, 68) 70–80 K towards higher temperatures as compared to that without the additive (R 3, 63) and the formation of $Ca(OH)_2$(s) and $Mg(OH)_2$(s), CaO_2(s) and MgO_2(s), CaO(s) and MgO(s) as solids and NO(g) (R 27–29, R 69–71) 20–50 K towards lower temperatures (Table 4, Figs. 3a, 4).

The temperature of probable NO_2(g) formation is increased, depending on the solid compound formed, 40–100 K towards higher temperatures (R 30–33, R 85–88) (Table 4, Fig. 3b).

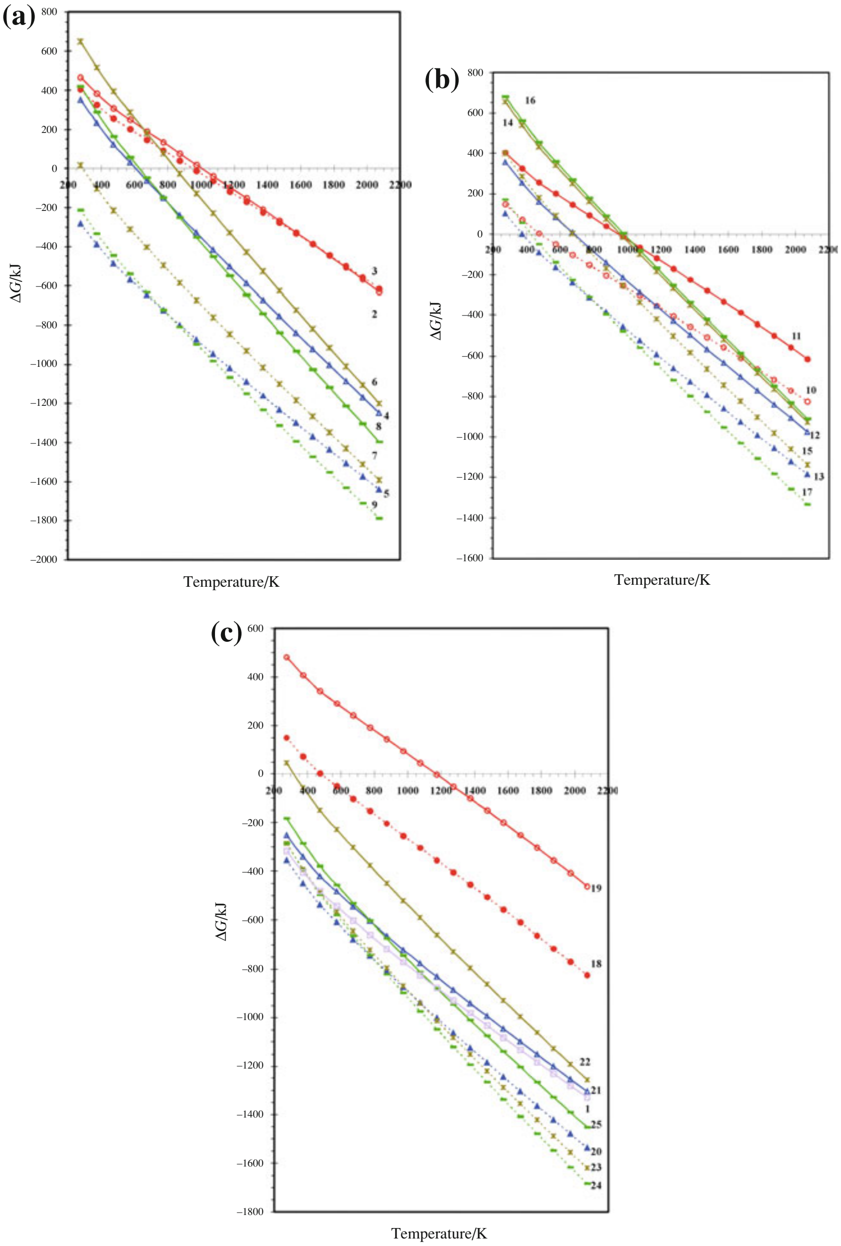


Fig. 3 Temperature dependencies of Gibbs free energy changes ΔG_T in the system $2NH_4NO_3$–$CaCO_3$ with formation of NO (**a**) (reactions 2–9), NO_2 (**b**) (reactions 10–17) and N_2O (**c**) (reactions 1, 18–25)

The $N_2O(g)$ formation together with $Ca(OH)_2(s)$ and $Mg(OH)_2(s)$ $CaO_2(s)$ and $MgO_2(s)$ CaO(s) and MgO(s) (R 35–37; R 106–108) is probable at room temperature, however, these reactions are less probable (*ΔG_T* values are higher) as compared to those in the system without the $CuSO_4$ additive (R 21, 22, 25; R 99, 101, 104). The temperature at which the reactions with the formation of Ca, Mg-nitrates in the additive-containing system becomes probable is moved in the system 2AN–0.5$CaMg(CO_3)_2$ 130 K (R 98, 105) and in the system 2AN–$CaCO_3$ 170 K (R 19, 34) towards lower temperatures–respectively, to 1050 K and 1000 K (Table 4, Fig. 3c).

$H_3BO_3(s)$ additive (0.5 mol) in the system 2AN–$CaCO_3$ and 2AN–0.5$CaMg(CO_3)_2$, practically, does not influence the temperature dependencies of ΔG_T of the reactions between AN and $CaCO_3(s)$ or $CaMg(CO_3)_2(s)$ with the formation of solid Ca,Mg-nitrates and NO(g) (R 38, 3; R 72, 63), but in the case of formation of $Ca(OH)_2(s)$ and $Mg(OH)_2(s)$ $CaO_2(s)$ and $MgO_2(s)$ CaO(s) and MgO(s) (R 40–42, 4, 6, 8; R 73–75, R 64–66), the temperatures at which these reactions become probable are decreased by 170–260 K (Table 4, Figs. 3a, 4).

The formation temperatures of $NO_2(g)$ are decreased by 30 K (R 43, 45–46, 11, 14, 16; R 85, 87–88, 80, 83–84)

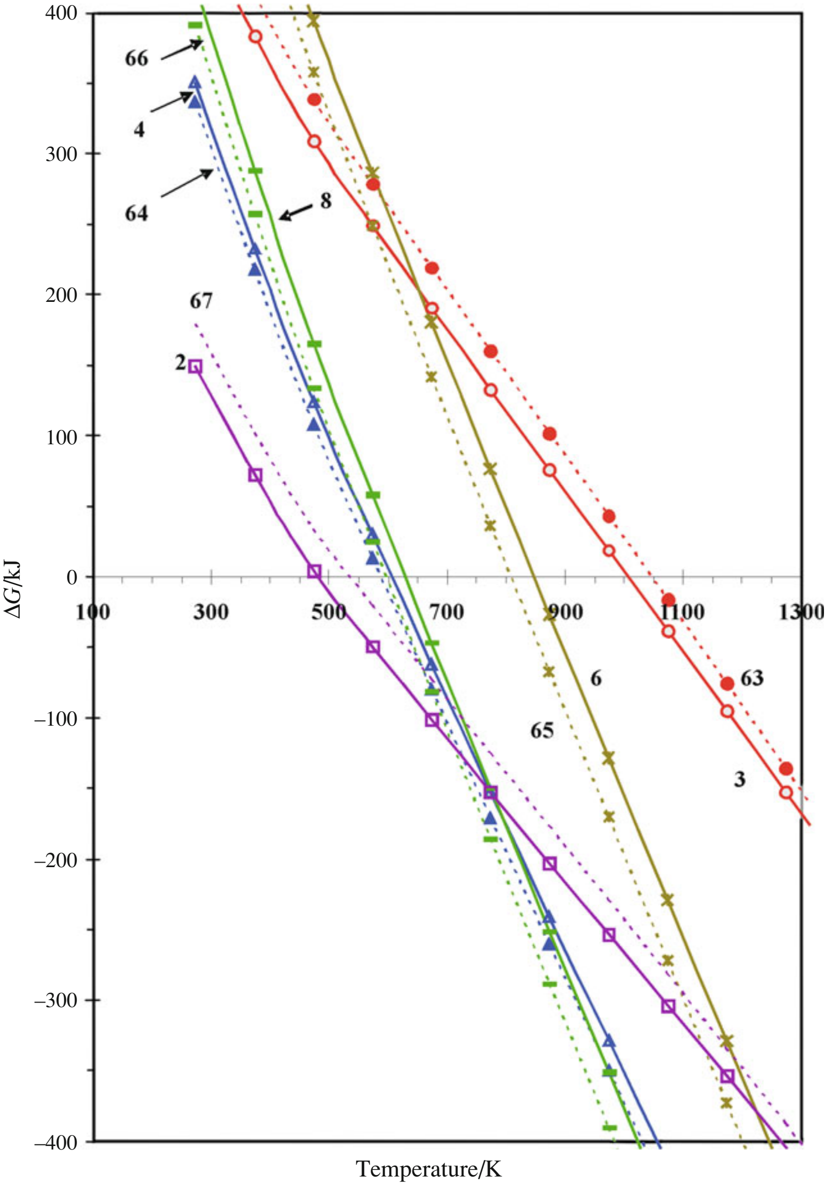


Fig. 4 Temperature dependencies of Gibbs free energy changes ΔG_T in the systems $2NH_4NO_3$–$CaCO_3$ and $2NH_4NO_3$–$0.5CaMg(CO_3)_2$ with formation of NO (reactions 2–4, 6, 8, 63–67)

except for the reactions with Ca,Mg-hydroxides formation (R 40, 12; R 90, 82) in the case of which these are shifted 20–30 K towards higher temperatures (Table 4, Fig. 3b).

The N_2O(g), and $Ca(NO_3)_2$(s), and $Mg(NO_3)_2$(s) formation in the presence of H_3BO_3(s) can take place at 700 K (R 47) instead of 1170 K (R 19) as in the system 2AN–$CaCO_3$ and at 750 K (R 109) instead of 1210 K (R 98) as in the system 2AN–$0.5CaMg(CO_3)_2$ (Table 4, Fig. 3c). The formation of the other solid phases studied can occur at room temperature (R48–50; R 110–112), however, these reactions are less probable as compared to these in the system without the boron additive (R 21–22, 25; R 99, 101, 104).

MnO_2(s) additive (0.5 mol) in the system 2AN–$CaCO_3$ and 2AN–$0.5CaMg(CO_3)_2$ moves the temperatures of NO(g) formation together with $Ca(NO_3)_2$(s) and $Mg(NO_3)_2$(s) 70–80 K in the direction of higher temperatures (R 51, 3; R 76, 63) and with $Ca(OH)_2$(s) and $Mg(OH)_2$(s); CaO_2(s) and MgO_2(s); CaO(s) and MgO(s) 60–70 K towards lower temperatures (R 52–54; R 77–79) as compared to the temperatures without manganese dioxide additive in the system (R 4, 6, 8; R 64–66) (Table 4, Figs. 3a, 4).

The temperature of probable NO_2(g) formation with $Ca(NO_3)_2$(s) as the solid product in AN–$CaCO_3$ system is increased up to 320 K (R 55, 11) and of the formation of the other solid phases under consideration by 40–70 K towards higher temperatures (R 56–58, 12, 14, 16; R 93–96, 80, 82–84) (Table 4, Fig. 3b).

In the presence of the additive, the temperature of the probable formation of N_2O(g) and Ca, Mg-nitrates(s) is shifted by 160 K in 2AN–$0.5CaMg(CO_3)_2$ system (R 113, 98) and by 200 K in 2AN–$CaCO_3$ system (R 59, 19) in the

Table 4 The influence of $CuSO_4$, H_3BO_3 and MnO_2 additive on the change in temperature/$\pm$ ΔT/K/at which reactions in the system 2AN–$CaCO_3$ and 2AN–0.5$CaMg(CO_3)_2$ become thermodynamically probable

System	N-containing gaseous compound		
Solid compound	NO	NO_2	N_2O
2AN + $CaCO_3$ + 0.5$CuSO_4$			
$Ca(NO)_3$	+80	+80	−170
$Ca(OH)_2$	−30	+90	At room temperature,
CaO_2	−50	+50	But less probable
CaO	−30	+50	Than without additive
2AN + 0.5$CaMg(CO_3)_2$ + 0.5$CuSO_4$			
$Ca(NO)_3$, $Mg(NO)_3$	+70	+90	−130
$Ca(OH)_2$, $Mg(OH)_2$	−20	+100	At room temperature,
CaO_2, MgO_2	−40	+70	But less probable
CaO, MgO	−30	+40	Than without additive
2AN + $CaCO_3$ + 0.5H_3BO_3			
$Ca(NO)_3$	+10	−30	−470
$Ca(OH)_2$	−190	+30	At room temperature,
CaO_2	−260	−20	But less probable
CaO	−180	−20	Than without additive
2AN + 0.5$CaMg(CO_3)_2$ + 0.5H_3BO_3			
$Ca(NO)_3$, $Mg(NO)_3$	~0	−30	−460
$Ca(OH)_2$, $Mg(OH)_2$	−180	+20	At room temperature,
CaO_2, MgO_2	−210	~0	But less probable
CaO, MgO	−170	−20	Than without additive
2AN + $CaCO_3$ + 0.5MnO_2			
$Ca(NO)_3$	+80	+320	−200
$Ca(OH)_2$	−70	+70	At room temperature,
CaO_2	−70	+50	But less probable
CaO	−60	+40	Than without additive
2AN + 0.5$CaMg(CO_3)_2$ + 0.5MnO_2			
$Ca(NO)_3$, $Mg(NO)_3$	+70	+70	−160
$Ca(OH)_2$, $Mg(OH)_2$	−70	+40	At room temperature,
CaO_2, MgO_2	−60	+60	But less probable
CaO, MgO	−70	+50	Than without additive

direction of lower temperatures–from 1170 to 970 K and from 1210 to 1050 K, respectively (Table 4, Fig. 3c). The solid phases like $Ca(OH)_2$(s) and $Mg(OH)_2$(s); CaO_2(s) and MgO_2(s); CaO(s) and MgO(s) can form at room temperature (R 60–62; R 114–116), but these reactions are also less probable as compared to those in the system without MnO_2 additive (R21–22, 25; R 99, 101, 104).

Conclusions

Thermodynamic analysis of the systems of AN with and without Ca and Mg carbonates with and without the presence of $CuSO_4$, H_3BO_3 or MnO_2 additive was carried out using the HSC software and getting the basics for future TA-measurements.

The list of the main compounds and their content in the equilibrium mixtures do not depend notably on the origin of Ca,Mg-carbonates. The main solid compounds that can form in the systems of AN and Ca,Mg-carbonates are $Ca(NO_3)_2$(s) and $Mg(NO_3)_2$(s); $Ca(OH)_2$(s) and $Mg(OH)_2$(s); CaO_2(s) and MgO_2(s); CaO(s) and MgO(s) and N-containing gaseous compounds NO(g), N_2O(g) and NO_2(g), the yield of which reaches 10^{-7}–10^{-5} mol. In the case of addition of H_3BO_3(s), MnO_2(s) or $CuSO_4$(s) into the system, the content of CuO(s), Cu_2O(s) or MnO(s) and SO_2(g), SO_3(g) or HBO(g) reaches the same level. Thereby, their equilibrium concentrations do not depend on the origin of the carbonate–$CaCO_3$(s), $MgCO_3$(s) or $CaMg(CO_3)_2$(s).

At constant temperature, the equilibrium amount of gaseous compounds does not depend on the content of carbonates (from 0.2 to 2.1 mol in the system) at the constant amount of AN (2 mol).

The reactions of AN and $CaCO_3$(s) or $CaMg(CO_3)_2$(s) with the formation of NO(g), NO_2(g) or N_2O(g) with the simultaneous formation of N_2(g) are more probable than those without N_2(g) formation and most of these reactions are probable at room temperature or at temperatures over 373–473 K. In the system of AN and $CaMg(CO_3)_2$(s), the temperatures at which these reactions become probable are shifted 20–50 K towards lower temperatures, except for the reactions with the formation of solid Ca, Mg-nitrates which become probable at 30–80 K higher temperatures as compared to the AN–$CaCO_3$ system.

Practically, the amount of 0.01 or 0.05 mol of $CuSO_4$(s), H_3BO_3(s) or MnO_2(s) additive in the system does not influence the temperature dependencies of ΔG_T of the reactions between AN and $CaCO_3$(s) or $CaMg(CO_3)_2$(s). The influence of additives taken in the amount of 0.5 mol was evident and, depending on the additive and the reaction, shifted their proceeding temperatures in the lower or higher direction even more than 300–400 K.

So, the information revealed can be used as fundamental data for applied aims—for the selection of suitable additives and their optimum amounts to obtain a stable non-explosive final product.

Acknowledgements This work was supported by the Estonian Ministry of Education and Research (SF0140082s08), the Estonian Science Foundation (G7548).

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