Ammonium nitrate explosions: answers

Education in Chemistry
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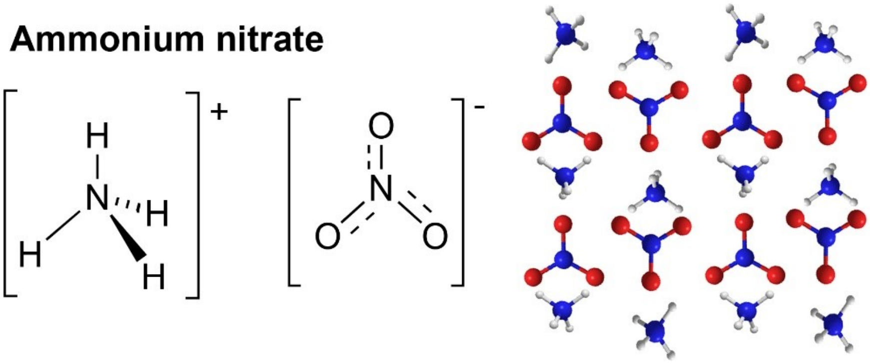
The decomposition of ammonium nitrate at temperatures above 260°C leads to a 'runaway' explosive reaction. Many aspects of this 'runaway' reaction can be explained by concepts such as enthalpy change and by taking a closer look at the structure and bonding of ammonium nitrate.

Task 1 – Structure and bonding in ammonium nitrate

The structure and geometry of ammonium nitrate are shown in the diagrams below.



1. Ammonium nitrate is composed of two polyatomic ions – identify the different type(s) of bonding within its structure.

Covalent bonding within NH_3 molecule
Coordinate bond between N and H^+ ion
Ionic bonding between NH_4^+ and NO_3^- in the lattice

2. Using the VSEPR theory and the diagrams above, state and explain the geometries of the NH_4^+ and NO_3^- ions shown.

NH_4^+ has four bond pairs which repel equally to give a tetrahedral geometry and a bond angle of 109.5˚.
NO_3^- has three double bond pairs which repel equally to give a trigonal planar geometry and a bond angle of 120˚.

Task 2 – Decomposition or explosion?

Pure ammonium nitrate does not explode easily and can be handled safely. It decomposes at 230°C producing nitrous oxide gas (N_2O) and water vapour.

3. Give a balanced equation for the decomposition reaction.

$NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(g)$

Above 260°C, if confined and when contaminated, ammonium nitrate will explode forming toxic gases such as NO_2, responsible for the 'orange brown fireball' described in the article.

The following equation represents one of the reactions contributing to the explosion:

$$4NH_4NO_3(s) \rightarrow 3N_2(g) + 2NO_2(g) + 8H_2O(g)$$

4. Given that the molar gas volume is 24.5 dm^3 at 298K and 1atm calculate the total volume of gas produced from 80 kg of $NH_4NO_3(s)$ under these conditions.

4 moles $NH_4NO_3(s) \rightarrow$ 13 moles of gas
1 mole $NH_4NO_3(s) \rightarrow$ 13/4 moles of gas
80kg $NH_4NO_3(s)$ = 1000 moles $NH_4NO_3(s)$ $\rightarrow$ 3250 moles of gas
Volume of gas = 3250 x 24.5 dm^3 = 79,625 dm^3

5. Use your value to calculate the total volume of gas at the same pressure and 300°C.
Scale this up to calculate the vast volume of gas produced from 2750 tonnes of $NH_4NO_3(s)$ in the Beirut explosion.

80kg $NH_4NO_3(s) \rightarrow$ 79,625 dm^3 of gas at 298 K
$V_1/T_1 = V_2/T_2$; 300°C = 573 K
79,625/298 = V_2/573; V_2 = 153,104.4 dm^3
2750 tonnes $\rightarrow$ 153,104.4/80 x 2750 x 1000 dm^3 of gas = 5,262,965.3x10^3 dm^3 of gas

Task 3 – Calculating the enthalpy of reaction, ΔH_R, and using kinetic theory to explain why this is a 'runaway' reaction

The data below will be used in Tasks 3 - 5

Compound	**ΔH^0f / $KJmol^{-1}$**	**$S^0/JK^{-1}mol^{-1}$**
NH_4NO_3 (s)	-365.6	+15.1
$N_2(g)$	0	+153.3
$NO_2(g)$	+33.2	+240.1
$H_2O(g)$	-241.8	+188.8

Once decomposition begins a 'runaway' reaction occurs. In a runaway reaction an exothermic reaction goes out of control. The heat evolved raises the temperature of the reacting mixture leading to an increase in reaction rate, which causes a further increase in temperature and a further increase in reaction rate until an explosion occurs.

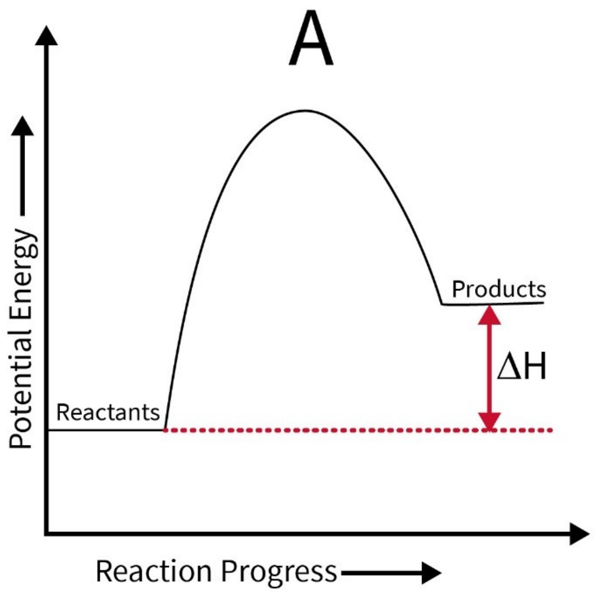
6. Use the standard enthalpies of formation, ΔH^0f**,** given in $KJmol^{-1}$ to calculate the enthalpy change for the reaction and confirm that it is exothermic

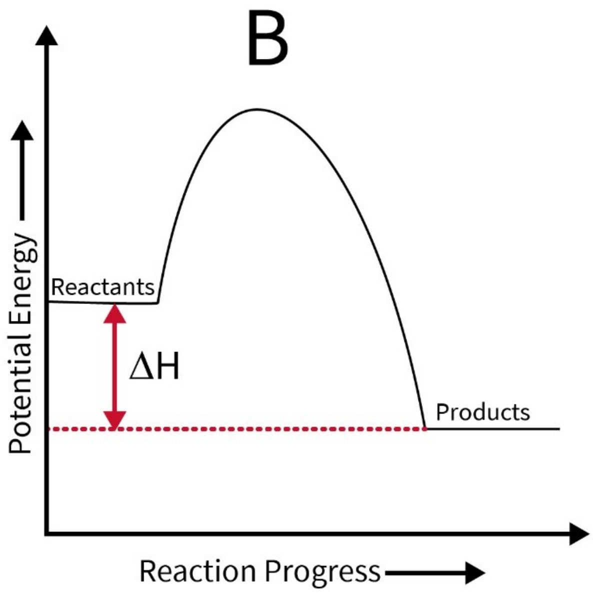
$$4NH_4NO_3(s) \rightarrow 3N_2(g) + 2NO_2(g) + 8H_2O(g)$$

ΔH_R = sum of (ΔH^0f products) **-** *sum of (ΔH^0f reactants)*
ΔH_R = -1934.4 + 66.4. + 1462.4 = - 405.6 $KJmol^{-1}$

7. Select which of the energy profile templates below (A or B) correctly represents the enthalpy change you have calculated and label it showing reactants, products, ΔH_R and E_{act}.

Energy profile diagram B, showing reactant, NH_4NO_3 , on LHS and products $3N_2(g)$,$2NO_2(g)$ and $8H_2O(g)$ on RHS. E_{act} shown as the difference in energy between reactants and peak of profile.





8. Use kinetic theory to explain why an increase in temperature causes an increase in reaction rate.

For a successful collision molecules need E > or = E_{act}. As temperature increases kinetic energy of molecules increases and more molecules have E > or = E_{act} resulting in more successful collisions per unit time.

Task 4 – Calculating the entropy change, ΔS, for the reaction

The changes in state during the decomposition reaction below suggest there will be a significant increase in the disorder, entropy, for the reaction – ie ΔS will be highly positive.

9. Use the standard entropies, S^0, given in $JK^{-1}mol^{-1}$ to confirm this is the case.

$$4NH_4NO_3(s) \rightarrow 3N_2(g) + 2NO_2(g) + 8H_2O(g)$$

ΔS = sum of (S^0 of products) - sum of (S^0 of reactants) = 459.9 + 1510.4 + 480.2 - 60.4 = +2390.1$JK^{-1}mol^{-1}$

Task 5 – Assessing the spontaneity of the reaction

To assess the spontaneity of a reaction both enthalpy and entropy changes need to be considered together in Gibb's Equation.

Using your enthalpy and entropy changes from Tasks 3 and 4 and Gibbs equation below:

10. Comment on whether the decomposition reaction is likely to be spontaneous at all temperatures.

Since ΔH = -ve and ΔS = +ve, both the terms ΔH and TΔS will be -ve at all temperatures above 0K; therefore ΔG = -ve indicating a spontaneous reaction.

11. Using temperatures of 300^{0}C and 500^{0}C in a model calculation comment on whether the decomposition is likely to become more favourable as the temperature increases.

At 300K: ΔG = -405.6 - 573 x (2390.1/1000) = -1775.1$KJmol^{-1}$
At 500K: ΔG = -405.6 - 773 x (2390.1/1000) = -2253.1$KJmol^{-1}$
ΔG becomes more -ve as T increases; therefore decomposition reaction becomes more favourable.

Reminders about Gibbs equation:

$$\boxed{\mathbf{\Delta} G = \mathbf{\Delta} H - T\mathbf{\Delta} S}$$

For a reaction to be spontaneous ΔG must be negative.
Take care with units!
ΔG and ΔH in $KJmol^{-1}$, ΔS in $JK^{-1}mol^{-1}$ and T is in K.