

Thomas Caswell Chemistry Assignment

by Thomas Caswell

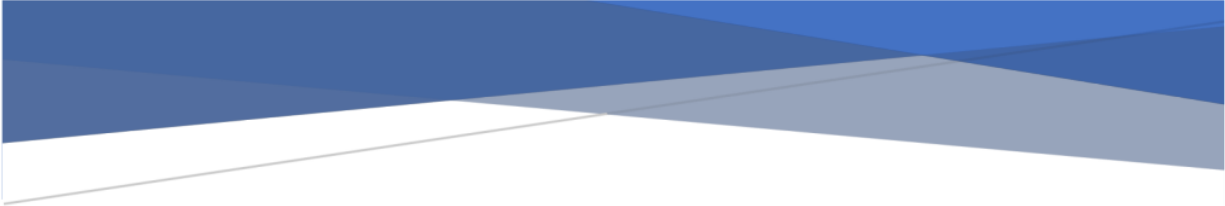
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THE DETRIMENTAL EFFECT OF WATER ON EXPLOSIVE MATERIALS & ORDNANCE MUNITIONS AND EXPLOSIVE (OME) RELATED PROCESSES

ACDA 4011 Chemistry Assignment

Abstract

This report describes the physical and chemical properties of water and links them to detrimental effects of water ingress in OME related processes. These include the sensitizing and desensitising of five primary and secondary explosive chemical compounds (mercury fulminate, lead azide, lead styphnate, nitrocellulose and 2,4,6-trinitrophenol) and how looking at corrosion chemical half equations could provide information on the creation of volatile metal salts from 2,4,6-trinitrophenol.

2479 words

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1. Introduction

This report begins with describing physical and chemical properties of water. These properties will then be linked to the effects of water on the explosive properties of mercury fulminate, lead azide, nitrocellulose and 2,4,6-trinitrophenol (or picric acid). Findings will then be concluded with suggestions on further work to be done by the student.

2. Physical & Chemical Properties of Water

2.1 Water Molecular Structure and Geometry

Water, or dihydrogen oxide, is a molecule composed of two hydrogen and one oxygen atom to make the chemical formula H_2O .



Figure 1: Ball & stick & Van der Waals graphical representations of water [1].

There are six outer valence shell electrons in the oxygen atom ($1s^2, 2s^2, 2p^4$). For it to obey the “octet rule” oxygen can gain two electrons to make its outer valence shell filled with eight electrons by forming two sigma (σ) covalent bonds with two hydrogen atoms ($1s^1$) [2]. Figure 2 shows the Lewis structure of water:

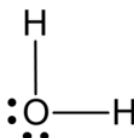


Figure 2: The Lewis Structural Representation of water [2].

The Lewis structure of water shows that there are two lone pair of electrons that are not involved in the bonding of the molecule. The Valence-Shell Electron Pair Repulsion model (VSEPR) considers the repulsive forces between pairs of valence electrons, including bonding pairs and lone pairs, and assumes that these valence electrons will influence the molecular geometry. The application of VSEPR to the water molecule gives it a tetrahedral arrangement with a bonding angle (α) of 104.5° [2]:

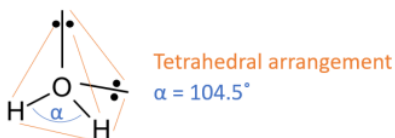


Figure 3: Application of VSEPR to water [2].

2.2 Dipole Moment & Solvation of Acids

Due to the difference in electronegativity between oxygen (3.5) and hydrogen (2.1) this polarises the two O-H bonds. The bent geometry of the overall molecule creates a net dipole of 1.85 D [2]. This means that the oxygen side of the molecule has a slightly negative charge (δ^-) and the hydrogen side of the molecule has a slightly positive charge (δ^+):

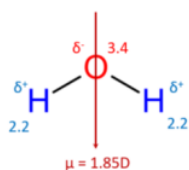


Figure 4: Net dipole moment of water is 1.85 D [2].

This gives it the ability to form weak intermolecular bonds with other organic molecules containing polarised covalent bonds, such as glucose (Figure 5). When understanding the interaction of water with organic molecules it is important to realise the polarity within and over the entire molecule.

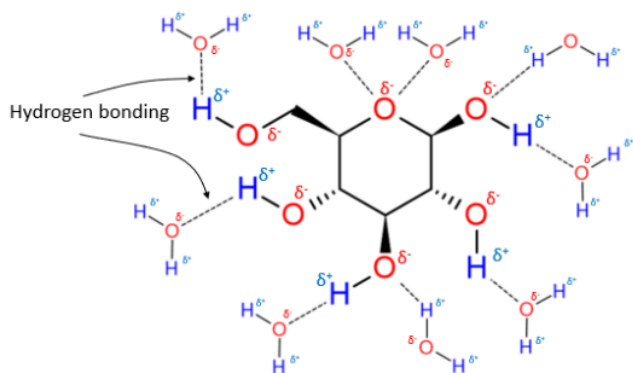


Figure 5: Structure of glucose showing how the polarised hydroxyl bonds and the ester oxygen can hydrogen bond with water; resulting in glucose being soluble in water [3].

Water also can solvate inorganic ionic compounds, such as potassium chloride (Figure 6), enabling it to be a solvent for these chemical compounds. The structure formed is known as a Lewis acid-Lewis base complex [2].

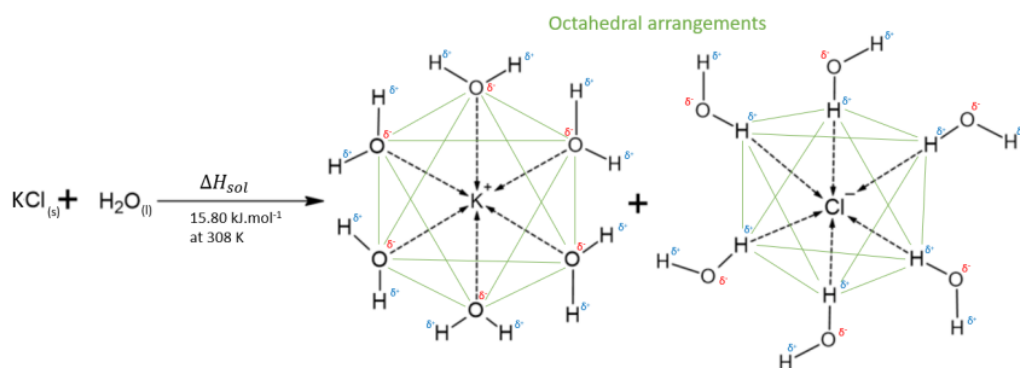
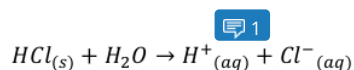


Figure 6: Solvation of KCl in water [2] [4].

An interesting point is that the solvation of chemicals such as the inorganic solid hydrogen chloride (HCl):



Equation 1: Solvation of HCl in water [5] [2].

Hydrogen chloride is a white covalent solid but when dissolved in water the polarised HCl bond is broken to yield hydrogen and chloride ions in solution. The hydrogen ion is otherwise known as a proton donor and acts as an acid, raising the pH of the water. Realising that water can activate some chemical compounds to become acidic and raise the pH of their environment is an important interaction to realise that could have consequence for ordnance, munitions, and explosive (OME) processes. 

2.3 Hydrogen Bonding

A hydrogen bond is defined as an interaction between a hydrogen atom attached to an electronegative atom and an electronegative atom that possesses a lone pair of electrons. [2] [6]. Water fits this definition, so forms this type of intermolecular bonding (Figure 7).

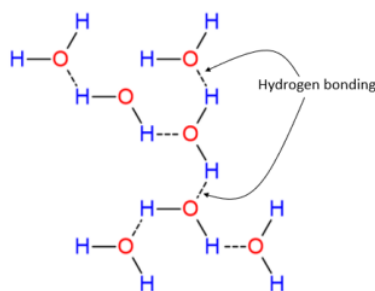


Figure 7: Cohesive hydrogen bonding in water [6].

When comparing Group 6 hydride boiling points (Figure 8) it is possible to observe that water has a relatively high boiling point (~360 K) compared to the other molecules (200 – 280 K). This is in part due to the strong amount of hydrogen bonding taking place in its liquid state [5]. A hydrogen bond has a bond strength of ~25 kJ mol⁻¹, for appreciation covalent bonds are normally in the range of several hundreds of kJ mol⁻¹ [2].

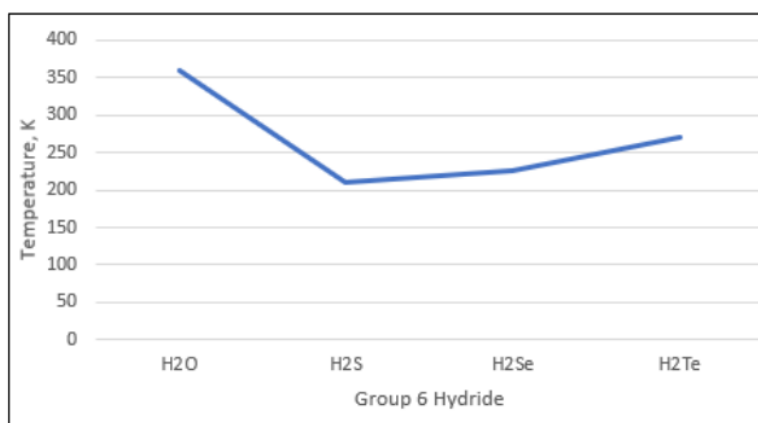


Figure 8: Boiling points of Group 6 hydrides [3].

2.4 Phases of Water

Water exists in three different phases. This can be seen in a heating curve beginning with a constant solid mass of H₂O until it is fully vapourised (Figure 9) [2].

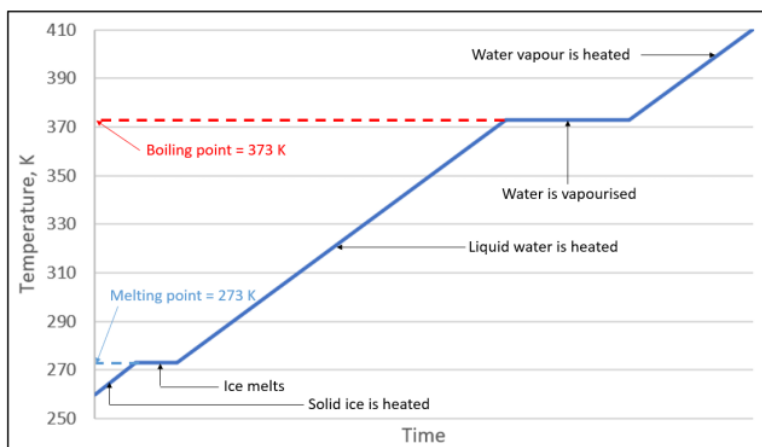


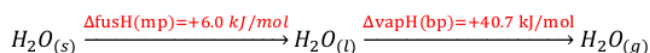
Figure 9: Heating curve for H₂O [2].

From the heating curve we can determine the melting point (T_m) and the boiling point (B_p). It is also possible to determine the specific heat capacity of water in the three different phases (Table 1).

Characteristic	Value
T_m	273 K or 0 °C
B_p	373 K or 100 °C
Specific Heat Capacity of H ₂ O _(s) or ice	2.03 J K ⁻¹ g ⁻¹
Specific Heat Capacity of H ₂ O _(l)	4.18 J K ⁻¹ g ⁻¹
Specific Heat Capacity of H ₂ O _(g) or vapour	1.97 J K ⁻¹ g ⁻¹

Table 1: Physical characteristics of H₂O [2].

The higher specific heat capacity of water as a liquid compared to a solid and gas shows that more heat energy is required to raise the temperature per unit mass. This indicates a greater degree of hydrogen bonding in the liquid state than in solid or gas.



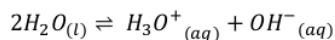
Equation 2: Molar enthalpy of fusion and vaporisation of H₂O [2].

The higher value for the molar enthalpy of vaporisation, $\Delta_{vap}H(bp)$, than the molar enthalpy of fusion $\Delta_{fus}H(mp)$ (Equation 2), also shows that more energy per mole is required for the endothermic process of the liquid to gas phase change than for the solid to liquid phase change. This again indicates more hydrogen bonding is needed to be overcome in liquid water.

Altogether this information shows the high degree of hydrogen bonding that occurs in liquid water ensures a large liquid temperature range. With regards to explosives, water is a product of the oxidation of hydrogen produced in an explosive reaction. The amount of heat energy that water molecules can contain is an important feature concerning the water-gas equilibrium and can have consequences for the force of the explosion [7].

2.5 Resonance and Self-Ionisation of Water

The self-ionisation constant, K_w , for water is 1.0×10^{-14} at 298 K. This means that a very small amount of water ionises [2]. Equation 2 shows how this ionisation is possible:



Equation 3: Resonance/self-ionisation of water [2] [8].

This property of water is an important feature in understanding its chemistry and how it interacts with other chemical compounds under varying conditions. Water can act as a proton donor and acceptor [8].

2.6 Water can as a Nucleophile

A nucleophile is an ion or molecule that can donate electrons or is “electron rich,” it then seeks to attack and react with positively charged, δ^+ or “electron deficient” parts of another molecule [8].

Together with the knowledge of dipole, resonance and that water possesses lone pairs of electrons. It can now be appreciated that water can act as a nucleophile as it does in the oxidation of alkenes to alcohols (Figure 10).

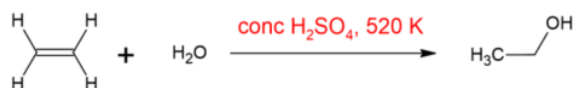


Figure 10: Addition of H_2O to alkenes in the formation of alcohols [2].

The mechanism by which the lone pair of electrons on the water attach the electron deficient site in the protonated alkene can be seen in Figure 11.

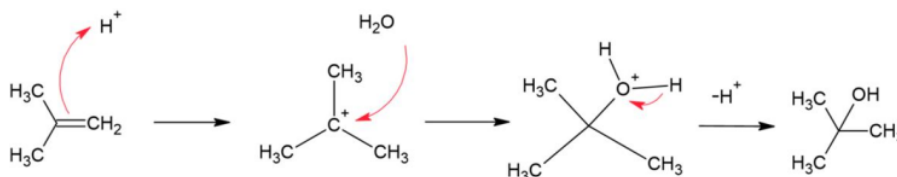


Figure 11: An example of nucleophilic attack by a water molecule [2].

This knowledge of organic chemistry may be useful in appreciating the effect of water on large organic molecules (polymers and aromatics) such as those used in OME.

2.7 Corrosion/Redox Chemistry

Water is a bad conductor of electricity, but in the presence of a salt or acid it becomes an electrolyte. An electrolyte is an electrically conductive solution that must be present for corrosion to occur [9].

Four components are required for corrosion to occur:

1. Anode
2. Cathode
3. Electrolyte
4. Metallic path

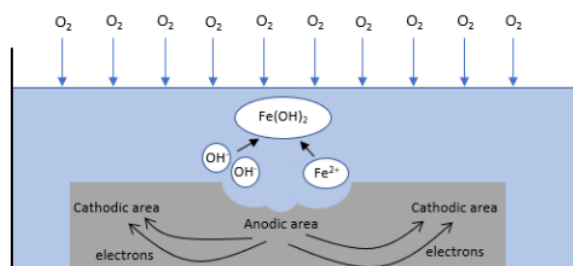
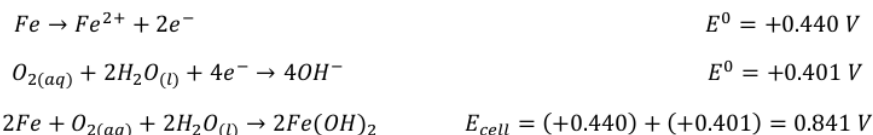


Figure 12: Formation of rust as an example of corrosion that can occur in the presence of water [9].

Half equations can show the ions that are formed as part of the redox chemistry for corrosion. They must occur in aqueous solution to occur; highlighting again the role water plays as for ionic compounds in section 2.2.

The half-cell reaction at the anode, cathode and combined is:



Equation 4: Redox chemistry for the corrosion of iron-based metals [9].

As the potential of the cell (E_{cell}) is positive therefore the reaction will proceed to the right if electron flow is maintained.

An important feature of corrosion is that it results in the dissolution of the metal anode. This means that the metal will degrade and lose its metallic properties. In a OME product this could lead to loss of function of metal containing components including switches, contacts, or metal additives. An example of metal additives is aluminium metal which is added to some explosives to increase blast pressure [7].

3. Detrimental Effect of Water on Primary Explosives

Akhavan's book states that water can have a detrimental effect on primary explosives. Water can also not have a detrimental effect, for example lead styphnate [7]. Primary or initiatory explosives are those that are sensitive to friction, shock, or heat [10]. Primary explosives appear to be compounds that are either ionic and/or inorganic having a metal ion as part of their chemical composition. From figure 4 in section 2.2, it is known that water can hydrate inorganic ionic compounds. Therefore, water ingress into OME items with these compounds could influence their explosive properties.

3.1 Mercury (II) Fulminate

Mercury (II) fulminate ($\text{C}_2\text{N}_2\text{O}_2\text{Hg}$) is an ionic compound with a central mercury cation combined with two fulminate anions.

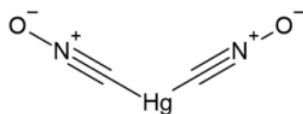
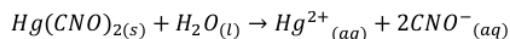


Figure 13: Graphical representation of mercury (II) fulminate [7].

Therefore, on contact with water this can dissociate as follows:



Equation 5: Solvation reaction of mercury fulminate.

Akhavan states that mercury fulminate is desensitised by the addition of water [7]. It could be that on dissociation into water the normal explosive chemistry between the ions in this compound is disrupted by the interference of the hydrogen bonding.

3.2 Lead Azide

Lead Azide (PbN_6) is another ionic compound that has a central lead cation combined with two azide anions. But with this compound Akhavan states that lead azide is unstable in the presence of moisture. This contrasts to the situation with mercury fulminate. One could presume that the presence of water could in fact speed up the explosive chemistry of this compound. One possible mechanism could be the ability of water to act as a nucleophile as described in section 2.6. It could be that the lone pair of electrons on the water atom interacts with the positive charge on the azide anions to enable the primary explosive to decompose easier.

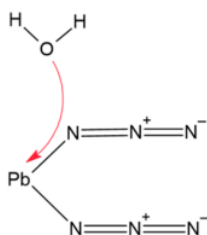
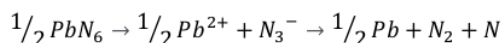


Figure 14: Lone pair of electrons attacking positive lead (II) centre in lead azide [7] [6].

Akhavan describes the first step of the reaction being:



Equation 6: Reaction scheme for the decomposition of lead azide [7].

This step is endothermic, meaning that it requires energy to proceed [8]. In this reaction the N_3^{-} anion is very unstable and expels a nitrogen atom out. This nitrogen reacts with another N_3^{-} anion to continue the decomposition of the primary explosive. Therefore, the presence of water dissociating the cations and anions perhaps enables the generation of the N_3^{-} anion. Leading to the reaction proceeding with less energy, thereby making the explosive decomposition more sensitive.

4. Detrimental Effect of Water on Secondary Explosives

Water can also have a detrimental effect on the performance of secondary explosives [7]. A secondary or high explosives are defined as explosives that detonate after the detonation of a primary explosive [10]. Again, it is possible to apply chemical knowledge from section 2 to understand the effects of water on these types of explosive chemical compounds. An observation from Akhavan's book is that secondary explosives tend to be larger organic molecules compared to primary explosives.

4.1 Nitrocellulose

Discovered in 1847 nitrocellulose is a polymer of beta glucose with each of the hydroxyl groups nitrated (Figure 15) [7].

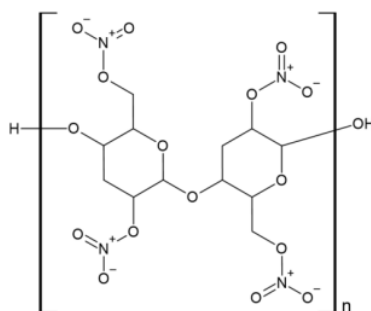


Figure 15: The chemical structure of nitrocellulose [7].

From the structure, one can observe that the polar ester oxygens are present as in Figure 5. There are also negative and positive charges on the attached nitrate groups. Therefore, it is possible to predict that nitrocellulose could form hydrogen bonds in water.

Akhavan states that nitrocellulose can be desensitised by the presence of water. Then like mercury fulminate perhaps the hydrogen bonding here like the dative bonding before is disrupting normal explosive chemistry from proceeding.

4.2 Picric Acid/2,4,6-Trinitrophenol

Discovered in 1742 picric acid is synthesised by the nitration of phenol. It has the following chemical structure:

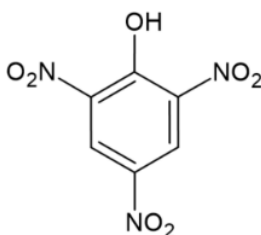


Figure 16: The chemical structure of picric acid [7].

Akhavan mentions that although it was used extensively as a military explosive in the late 1800s, it gave two problems that were related to the presence of water. The first problem was that like hydrogen chloride in section 2.2 the compound dissociates to create an acid (Figure 17) [7].

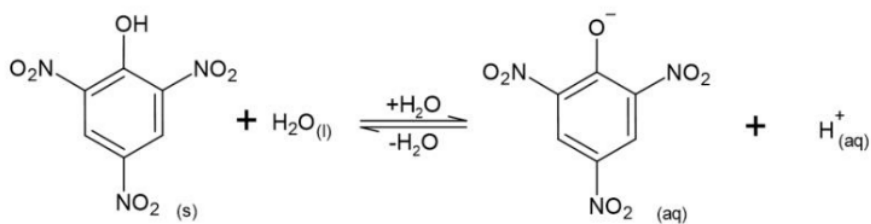


Figure 17: The solvation reaction of picric acid.

The presence of acid in a corrosive environment as detailed in section 2.7 has been shown to exacerbate the corrosion chemical process [9]. Corrosion of shells that use picric acid means that the

dissolution of the metal could lead to loss of shell structural integrity and potentially disrupting the normal OME processes related to this article.

The second issue that Akhavan mentions is that the metal salts of picric acid are more sensitive and prone to accidental initiation. The metal ion could be scavenged from the corrosion process and the salt would be developed from drying off water present.

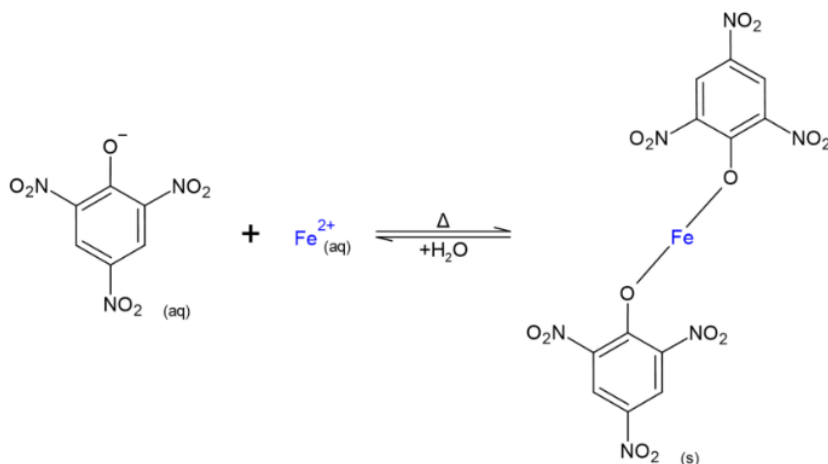


Figure 18: Proposed mechanism for the unintentional creation of picric metal salts during corrosion.

An observation of the picrate metal salt in Figure 18 could be that the structure now more resembles those of mercury fulminate and lead azide with a central metal cation electrostatically bonded to two organic anions species. Therefore, perhaps this could be linked to its explosive behaviour now being more like a primary explosive – being more prone to accidental shocks.

5. Conclusion

In conclusion, the chemical and physical characteristics of water have been studied in this report. They have then been linked to the effects of water ingress in two primary and two secondary explosive chemical compounds. Consistency has not been found in how the water affects the explosive properties of these compounds. Water has been found to desensitise and desensitise primary and secondary explosives.

Therefore, to limit the detrimental effects it can be acknowledged that correct explosive chemical material selection for an OME article would be important. Such as lead styphnate over mercury fulminate and lead azide in a water environment. Where selection of a chemical compound cannot be restricted then the engineering design, operations, and maintenance of the OME article to prevent water ingress would be critical.

6. Further Work

Further work for this student would be to look at the structure and possible interactions with water of more explosive chemical compounds to gain a wider knowledge of explosive chemical compounds.

A closer study of the thermal decomposition, thermos chemistry, equilibria, and kinetics of the various explosives would also likely yield further information on the effect of water on OME related processes.

It would benefit this student to look further beyond the chemical structures of explosive chemistry to the engineering level to see how water ingress is mitigated in OME articles.

References

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GRADEMARK REPORT

FINAL GRADE

GENERAL COMMENTS

Instructor

68/100

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Comment 1

to balance this equation and show the actual solvation ions it should be H_3O^+



Comment 2

what consequences specifically?

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PAGE 9

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PAGE 12

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THOMAS CASWELL

68

CRITERIA 1

(20%) Engagement with Literature Skills

properly cited, individually searched sources.

17

CRITERIA 2

(25%) Knowledge and Understanding Skills

no humidity mentioned. properties of water described but weakly related to the OMEgood level of knowledge demonstrated. conceptual knowledge demonstrated procedural knowledge - poor

16

CRITERIA 3

(25%) Cognitive and Intellectual Skill

OME problems mentioned but not discussed. only two problems discussed

15

CRITERIA 4

(20%) Practical Application Skills



the report does not include discussion of all the
papers mentioned in brief, lack of creative thinking
good report writing skills

12

CRITERIA 5

(10%) Transferable Skills for Life and Professional Practice



properly structured report, good word count

8