CHEMICAL REACTIONS IN HIGH- TEMPERATURE WATER USING MATHEMATICS AND PHYSICS CONCEPTS

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ABSTRACT:

A mathematical model for the primary chemical process occurring in 1 J/pulse electrical discharge in water has been developed. The discharge channel is divided into two zones: The core and recombination region. The core is a very narrow (ca 10 µm) part of the channel where high temperature initiation reaction take place and where the majority of molecule hydrogen and 47 % of the molecular oxygen are formed. The recombination region is a 200 µm radius zone where additional reactions such as hydrogen peroxide formation take place. The temperature in the core ranged from 5000 K at the centre to 2000 K at the boundary and the pressure. The only adjustable parameter in the system was found to be 14 atm. The model describes for the first time how molecular oxygen is formed in an underwater discharge and it is also able to described the experimental observed stoichiometry of H_2, O_2 and H_2O_2 formation. The concentration and temperature profiles inside the discharge channel as well as a general scheme for the water dissociation and molecular species formation are also reported. There have been few studies in the literature that closely examined the different potential influences of High temperature – water (HTW) on chemical reactions. Although the existing reviews and overviews of reactions in aqueous media include some discussion of solvent effects, in none of these reviews is the focal point the role of the reaction medium. This previous treatment of this topic is neither complete nor critical.

Keywords:

Chemical engineering, High temperature-water, Mathematical model, Stoichiometry

RESUMEN

Se ha desarrollado un modelo matemático para el proceso químico primario que ocurre en una descarga eléctrica de 1 J/pulso en el agua. El canal de descarga se divide en dos zonas: el núcleo y la región de recombinación. El núcleo es una parte muy estrecha (aproximadamente 10 µm) del canal. donde tiene lugar la reacción de iniciación a alta temperatura y donde se forma la mayoría de la molécula de hidrógeno y el 47 % del oxigeno molecular. La región de recombinación es una zona de radio de 200 µm donde tienen lugar reacciones adicionales como la formación de peróxido de hidrógeno. La temperatura en el núcleo osciló entre 5000 K en el centro y 2000 en el límite y la presión. Se encontró que el único parámetro ajustable en el sistema era 14 atm. El modelo describe por primera vez cómo se forma el oxígeno molecular en una descarga submarina y también es capaz de describir la estequiometría observada experimentalmente de la formación de H2, O2 y H2O2. También se informan los perfiles de concentración y temperatura dentro del canal de descarga, así como un esquema general para la disociación del agua y la formación de especies moleculares.Ha habido pocos estudios en la literatura que examinen de cerca las diferentes influencias potenciales del agua a alta temperatura (HTW) sobre reacciones químicas. Aunque las revisiones existentes y las descripciones generales de las reacciones en medios acuosos incluyen alguna discusión sobre los efectos de los solventes, en ninguna de estas revisiones el punto focal es el papel del medio de reacción. Este tratamiento previo de este tema no es completo ni crítico.

Palabras clave:

Ingeniería química, Agua a alta temperatura, Modelo matemático, Estequiometría.

I. INTRODUCTION

High-Temperature water (HTW) is liquid water above 200 ^{O}C and it is also supercritical water with temperature above 374 ^{O}C and pressure above 218 atm and is nowadays considered as a medium for organic chemistry. For that it requires the right combination of the chemistry and the reaction environment. Chemistry in HTW is important from both scientific and engineering standpoints. One example of that is the conversion of kerosene into petroleum and this occurs in the presence of clay minerals. High-Temperature water (HTW) can also be used for certain reactions such as chemical synthesis, materials synthesis, plastics recycling, coal liquefaction,

Waste destruction and biomass processing. This means, the use of HTW for these reactions has been motivated by the desire to create a cleaner, safer and more environmentally benign chemical processes.

To have maximum control over the HTW- mediated processes and also to exploit the properties of HTW, one must understand how the reacting system and water medium interact. One way in which they interact is that the water molecules can be involved in a reaction as reactants or as catalysts. Water can also influence the reaction in several ways such as cage effects, solute-solvent collisions, diffusion limitations and phase behavior.

In liquid water the solubility of most gases decreases as the temperature increases. But, the gas solubility increases as soon as the minimum is reached. Also from experiments it has been observed that HTW can support ionic, polar non-ionic and free-radical reactions. However, the relative rates of these classes of reactions can be sensitive to the reaction conditions, meaning that it can give rise to temperature and density effects on reaction kinetics.

Electrical discharges in water have been investigated for various purposes such as water treatment, microorganism destruction and the formation of shock waves. A pulsed electrical discharge in water produces conductive channels called streamers or streamers-like plasma channels. (Maria Amélia Jerónimo and José Alberto Rodrigues, 1998)

After being formed in a discharge channel ,these and other radical species either react with each other to form a product molecules, such as hydrogen and hydrogen peroxide, or diffuse away to react with solutes. System properties such as solution composition, applied voltage, P^{H} and conductivity play important roles in discharge channel formation and strongly affect the resulting radical concentration.

The overall stoichiometry of molecular species formed by pulsed electrical discharge in water follows the overall stoichiometry represented by reaction:

$$6H_2O \rightarrow 4H_2 + 2H_2O_2 + O_2 \quad (1)$$

The goal of this study is to develop a more realistic model that would consider the pulsed and inhomogeneous nature of the discharge, take into account temperature dependent chemical reactions and avoid the use of global reaction.

The reaction from radiolysis and electron beam studies could not simulate the correct formation of the hydrogen peroxide that was measured, and therefore additional reactions were added to the model including a global source of hydrogen peroxide in the form of reaction.

$$2H_2O \rightarrow H_2 + H_2O_2 \quad (2)$$

When the pulse is on, the set of reactions used to simulate the production of molecular species and radicals was taken from the NIST Chemical Kinetics database which compiles kinetics data on gas phase reactions. A thermal energy balance was also solved to determine the temperature distribution inside the streamer.

As a result, the model consists of a system a system of partial differential equations where the thermal energy balance is linked to the species balances via the temperature dependent reaction rates and diffusion coefficient. The system of equations was solved using the MATLAB 4.1 partial differential equation solver. The model neither does nor includes the global reaction as a source of hydrogen peroxide and oxygen but rather incorporate initiation reaction from thermal dissociation of water vapour. The model was developed with consideration of the production of hydrogen peroxide and oxygen as measured experimentally. (Brill,T.B.J, 1981)

1 .1 Description

The properties of HTW were determined with variety of experimental and computational techniques. The constant such as the dielectric constant (Є) and the ionic product (Kw) play a major role in the many properties of HTW. So is temperature and density as well.

The changes in the hydrogen bonding of HTW are accompanied by changes in the dielectric constant of water. That is increasing temperature and decreasing density decreases the dielectric constant (Є) In HTW carboxylic acids undergo hydrothermolysis not hydrolysis. Autocatalysis can also occur in the presence of carboxylic acids and mineral acids (**HX, HNO_3**) as reactivity of organic compounds in HTW. Increased density can favor hydrolysis whereas increasing temperature favors pyrolysis.

Studies cited in this section focus on supercritical systems. Effects of solute-solvent and solvent-solvent interactions can be pronounced in SCW because of its isothermal compressibility.

In solvent, the solute-solvent interaction modifies the free energy of activation (Equilibrium solvation effects) and the transmission coefficient (Non equilibrium solvation effects).

Equilibrium solvation effect is dominant on the rate constant when solvent molecules adjust rapidly enough to the changes in the reaction system. And when the solvent molecules cannot adjust to the change in reacting system rapidly enough to maintain equilibrium solvation.

In case of equilibrium solvation effects, the total free energy of activation can be separated into activation barrier for the reaction in the gas phase and the change in the activation due to the presence of the solvent.

A presence of a solvent such as water can influence a reaction in certain ways. It activates unimolecular reactions in gas-like environment by colliding with surrounding molecules. Thus, kinetics is influenced by the collision frequencies.

Reactions, which occur in liquid-like environment, are diffusion-controlled and their rate depends on the viscosity of the solvent. Thus, both collision and diffusion play a major role in kinetics of reactions (gas-like and liquid-like) in SCW. (Yaocihuatl Medina-Gonzalez, Séverine Camy and Jean-Stéphane Condoret 2014)

I.2 General Analysis

The mechanisms by which water generates a in what Hydrogen have been proposed, that the hydro cracking of polyethylene in HTW produced alcohols and ketones by Little char compared to the neat pyrolysis that water are converted to the corresponding ketones.

On the basis of the hydrogen balance of the product and the oxygen content in the char formed from isoquinoline pyrolysis and water liberates hydrogen by oxidizing the carbon component. The reaction of unsaturated nitriles in HTW can have a complex pathway, because the reactant has two functional groups that react with water. The saturated nitrile and amide undergo further hydrolysis reactions.

The quantum Chemical calculations revealed the role of water in formic acid decomposition .Formic acid decomposes through two pathways, dehydration and decomposition, both of which require intermolecular hydrogen transfer.

The response of non-ionic reaction to the changes in the dielectric constant and hydrogen bonding of water depends on the difference in the polarity between the reactant and transition state. If the transition state is more polar than the reactants a non-ionic reaction behaves just like an ionogenic reaction .This is, the rate increases with the increasing water density. The water gas-gas shift reaction proceeds via formic acid or formate intermediate, so it provides an example in which the transition is more polar than the reactants CO, H_2O.

The experimentally observed acceleration of hydrolysis in HTW with decreasing temperature ,increasing pressure , and increasing salt concentration supports the neutral hydrolysis mechanism .The literature suggests that the salvation effects are not negligible for free radical reactions ,even though the electrostatics interactions are much less significant for these

I.3 Properties Of HTW

The properties of HTW were determined with variety of experimental and computational techniques. The constant such as the dielectric constant (€) and the ionic product (Kw) play a major role in the many properties of HTW. So is temperature and density as well.

a) The pair correlation functions of liquid and supercritical water at constant pressure. The nearest-neighbor peak **(r∞~3Aº)** become smaller with increasing temperature and it moves toward larger distance. However the second-neighbor peak **(r∞~4.5 Aº)** becomes smaller as the temperature increases and it disappears.

b) The appearance of oxygen-oxygen correlation functions for supercritical water and liquid changes with temperature and density. That is the nearest-neighbor peak becomes larger as the density is increasing. Whereas, the second –neighbor peak becomes smaller and it disappears. These changes explain that as the density decreases, the HTW structure approaches that of simple gas.

c) The density decreases and the temperature increases, the hydrogen-bonding in water becomes weaker and less persistent.

d) In HTW, a reduced extend of hydrogen bonding exists that is at supercritical temperature and gas-like densities (~0.1g/cm^3)

e) The hydrogen-bond network in HTW exists in form of small clusters of Hydrogen-bonded water molecule. The size of these clusters decreases as the temperature increases and the density decreases

f) HTW is less ordered than ambient liquid water, but it retains some liquid water-like structure on a microscopic level.

g) The changes in the hydrogen bonding of HTW are accompanied by changes in the dielectric constant of water. That is increasing temperature and decreasing density decreases the dielectric constant (ε) of water. For example, the dielectric constant for 300 °C and 0,75 g/cm^3 is 21, whereas the one for 500 ºC and 0,30 g/cm^3 is 4.1.

The following empirical equation is used to correlate the experimentally measured dielectric constant (ε) for water with temperature and density.

$$\varepsilon=1+ (A1/T)\,\rho+ (A_2/T^o+A_3+A_4/T^o)\,\rho^2+ (A_5/T^o+ A_6T+ A_7T_2{}^o)\,\rho^3+ (A_8/T_2+ A_9/T+ A_{10})\,\rho^4 \quad \textbf{(3)}$$

Where

T^o is the normalized temperature

ρ is the normalized density

A_i is the fitting parameters

h) HTW has a low dielectric constant and thus it behaves more like polar organic solvents than ambient liquid water. Meaning, the dielectric constant (ε) for ambient liquid water is higher

i) The HTW also has a property of solubility. Small organic compounds are highly soluble in it.

j) As the temperature increases and the density decreases self-diffusivity of HTW also increases.

k) The ion product (Kw) of HTW varies with changes in temperature and density.

The following formula is used to correlate the experimentally measured Kw with temperature and density.

$$LogKw = A + \frac{B}{T} + \frac{C}{T2} + \frac{D}{T3} + \left(E + \frac{F}{T} + \frac{G}{T2}\right) \quad \textbf{(4)}$$

Where

T is the temperature (Kelvin)

P is the density (g/cm^3)

A-G is the fitting parameters

.

l) Another property of HTW is that dense HTW is very effective for acid-catalyzed and base-catalyzed reactions.

II. RESULTS.

2. Role Of Water In Chemistry

2.1 Water In Hydrolysis And Hydration

Hydrolysis of organic compounds in HTW can help

- Destroy organic compound or wastes.
- Recover valuable chemical resources (e.g. Recycling of plastic wastes).
- Provide source of chemical feed stocks

Table 1 shows below that organic compound are hydrolyzed to various degrees in HTW. E.g. compounds with a saturated carbon atom attached to a heteroatom-containing functional group are susceptible to hydrolysis.

Nitriles are first hydrated to form amides, which are then hydrolyzed.

Table 2 below summarizes the expected products for the hydrolysis of Ethers, esters, amides, amines, nitroalkane, and alkyl halides (e.g. **Carboxylic acids**)

2.2 Water As A Hydrogen Source

Experimental data (isoquinonline pyrolysis in SCWO hydrocarbon pyrolyses in supercritical D2O).Clearly depicts that water can supply hydrogen atoms in reactions in HTW.

Because of its hydrogen-donating ability, water can shift the selectivity of pyrolysis away from the formation of high molecular weigh (pyrolysis of guaiacol) in HTW. Water generates hydrogen by several mechanism

2.3 WATER IN FREE-RADICAL CHEMISTRY

Reactions in which water participates involves the formation or destruction of highly reactive free-radical intermediates.

E.g. hydroxyl is the most effective oxidant present during SCW, reactions (a result in hydrogen peroxide which will dissociates and for reactions, two additional OH radicals (H_2O_2=2OH), effectively generating three OH radicals from a single hydroperoxyl radical (HO_2) which is less reactive oxidant. (Savage, P.E, 1999)

Table 1 .Experimental studies of hydrolysis in HTW

Reactant
Ethers
Esters
Amides
Nitriles
Amines
Nitroalkane
Alkyl halide
Nylon
Poly (ethylene Terephthalate)
Polycarbonate
Phenolic resin
Epoxy resin
Cellulose
Chitin
Cellobiose
Glucose
Fructose
Vegetable oils

2.4 Water As A Catalyst

A water can be a source of catalyst that modifies and stabilizes the transition states in a form of an acid or base.

2.5 Water As Acid/Base Precursor

In HTW, the concentrations of H^+ and OH^- ions are naturally high facilitate acid/base catalyzed reactions e.g. Alcohol dehydration, hydrolysis.

E.g. Decomposition of methyl tert-butyl ether (MTBE)

Table 2. .Expected products from hydrolysis in HTW

Reactant	Reaction
Ethers	ROR'+H2O⇨ROH+R'OH
Esters	RCOOR'+H2O⇨RCOOH+R'OH
Amides	RCONH2+H2O⇨RCOOH+NH3
1^{ST} Amines	RNH2+H2O⇨ROH+NH3
2^{ND} Amines	RNHR'+H2O⇨ROH+R'NH2
3^{RD} Amines	RR'NR''+2H2O⇨ROH+R'OH+R''NH2
1^{ST} Nitroalkane	RCNO2+H2O⇨RCHO+HNO3
2^{ND} Nitroalkane	RCNO2R'+H2O⇨RCR'O+HNO3
Alkyl halides	RX+H2O⇨ROH+HX
1^{ST} Gem-dihalides	RCX2H+H2O⇨RCHO+2HX
2^{ND} Gem-dihalides	RCX2R'+H2O⇨RCR'O+2HX

RCHO⇨Aldehydes, RCR'O⇨Ketones

Notice:

In HTW carboxylic acids undergo hydrothermolysis not hydrolysis. Autocatalysis can also occur in the presence of carboxylic acids and mineral acids (HX, HNO_3) as reactivity of organic compounds in HTW. Increased density can favor hydrolysis whereas increasing temperature favors pyrolysis. (Mizan, T.I ;Savage, P.E; Ziff and R.M.J 1996)

2.6 Water As Catalyst In The Transition State

This type of catalysis is important for reactions involving some type of intra molecular hydrogen transfer as water molecules act as proton relay and facilitate thereby the formation and cleavage of bonds that lead to the products (e.g. Klein/Billz conversion of nitro-aniline to benzofurozan and decarboxylation of acetic acid derivatives in HTW).

Water molecules can catalyze a reaction by directly participating in the transition state and reducing its energy (Experiments of Melius et al predict activation energy in HTW should be approximately 20-30 Kcal/mol lower than the gas-phase value. (Keith.J.Laidler and John H.Meiser 2005)

3. Roles Of Intermolecular Interactions In Htw

Studies cited in this section focus on supercritical systems. Effects of solute-solvent and solvent-solvent interactions can be pronounced in SCW because of its isothermal compressibility.

Table 3. Summary of effects of water organic chemical reactions in HTW

Role of water	Applicable conditions	Affected reactions
Reactant/product	Any, but importance increases at higher water densities	Reaction in which water is reactant (e.g. hydrolysis, hydration, hydrogen abstraction
Catalyst	Any	Proton –transfer reactions in which water interacts with reactant(s), typically via hydrogen bonding
Acid/base catalyst Precursor	More important at higher temperature and liquid like densities	Acid/base-catalyzed reactions
Preferential solvation/ desolvation of transition state	Any, but probably less important at gas like densities	Reactions with change in solute-solvent interactions (e.g. electrostatic, hydrogen bonding, etc…) between reactant(s) and transition state, examples include reactions with a change in polarity along the reaction coordinate
Hydrophobic effect	More important at near-ambient conditions than in HTW	Condensation reactions with immiscible organic reactants
Solvent dynamics	More important at liquid like densities	Very fast reactions (faster than solvent reorganization)
Density inhomogeneities	Supercritical conditions	Any reaction can be affected by the local composition differing from the bulk composition.
Energy transfer	More important at gas like densities, energy transfer is not likely to be rate limiting	Nominally unimolecular elementary reactions
Cage effects	More important at liquid like densities	Bimolecular reactions (in either forward or reverse direction

3.1 Solvation Effects

In solvent, the solute-solvent interaction modify the free energy of activation (Equilibrium salvation effects) and the transmission coefficient (Non equilibrium solvation effects).

Equilibrium solvation effect are dominant on the rate constant when solvent molecules adjust rapidly enough to the changes in the reaction system. And when the solvent molecules cannot adjust to the change in reacting system rapidly enough to maintain equilibrium solvation.

In case of equilibrium solvation effects, the total free energy of activation can be separated into activation barrier for the reaction in the gas phase and the change in the activation due to the presence of the solvent. (Carlos Sarrico ,2002).

$$DE=DE_{gas}+DG_{Solid} \quad \textbf{(5)}$$

Assuming this reaction is identical in the gas phase and in HTW, we can express the rate constant in HTW.

$$Khtw/Kgas = e^{(-DGsolid/RT} \quad \textbf{(6)}$$

3.2 Effects Of Preferential Solvation

-The preferential salvation of the reactants or the transition-state species in water at different pressures/densities and temperature influence the kinetics of reactions in HTW.

In order to interpret these influences Klein and co-workers divided an overall activation volume into different parts.

E.g. electrostatic hydrolysis and diffusion.

-Quantum chemical calculation also revealed that a solvent compressibility also plays a role in the salvation effects on reaction kinetics. (Tangus Park and Pedro Lopes, 2007)

-Mostly reactions that involve change delocalization or localization (ion or polar nonionic reactions).Bring out effects of preferential salvation in HTW.

For example the effects of temperature and density or ionic and polar reactions in HTW causes the changes in the dielectric constant with temperature and density. This dielectric constant indeed is an indicator for the ability of water to solvate the reactants and transition states.

Ionic reactions have two classes, namely:

a) **1.**Ionogenic
b) **1.**Iso-coulombic

a) 1. Ionogenic reaction involves dissociation of a neutral molecule into charged species. This reaction increases with increasing dielectric constant. Effect of water density on the kinetics is larger.

b) 1. Iso-coulombic reaction

Effect of water density on the kinetics is generally small.

-Preferential salvation also has an effect on the SN2 reaction of Methyl Chloride and Chloride ions (CH_3CL+CL^-).This effect arise from the change in the polarity of the reactants,

-Due to salvation effect, the dielectric constant and hydrogen bonding in water affects the reactions and equilibrium of acid-base reactions. At the constant temperature, increasing the water density favors an increasing degree of change separation.

-Another effect of preferential salvation is that it causes water to provide different degrees of stabilization for different reactions, thus the reaction pathway for multistep reactions is altered. For example, during the decomposition of nitro methane. (Jędrzej Walkowiak, Giancarlo Franciò and Walter Leitner,2017)

*3.3 **Effect Of Hydrobicity***

Hydrophobic effect is a type of equilibrium solvation effect and organic solutes tend to have it to aggregate to minimize the water-organic interface.

The important condition at which hydrophobic effect arise is when the hydrocarbon solubility is decreased. Due to lower dielectric constant and fewer hydrogen bond, HTW exhibits higher solubility for organic compounds than ambient liquid water. Therefore, hydrophobicity has less effect on HTW than ambient liquid water. This is explained by the weaker potential mean force for benzene dimmer.

Here some of hydrophobic effect.

a. Due to the hydrogen-bond network of ambient liquid water, the water- organic interactions are less attractive and less strong than water –water interactions in high cohesive energy.

b. Hydrophobicity affects the kinetics of condensation-type organic reactions in water by bringing the reactants closer together. This results in water reducing the activation barrier for polar bimolecular reactions without reducing their dilution rate.

c. The selectivity of organic reactions in water is also slightly changed by hydrophobicity. It favors the product that is more compact. The effect of hydrophobicity on condensation –type organic reactions was first discovered by Breslow and co-workers on Diels-Alder reactions in ambient liquid water. Example of Diels-Alder reactions is the reaction of Cyclopentadiene with butanone in water.
Cyclopentadiene with Butanone in isooctane.

Cyclopentadiene with Butanone in methanol.

*3.4 **Effect Of Solvent Dynamics***

In some reactions, there are substantial changes in the electronic structure of the reactants. A solvent which is also involved in a reaction then respond dynamically to these changes and this affects the kinetics of the reaction. If the solvent fails to maintain the equilibrium solvation by adjusting to these changes, this may produce barrier recrossings due to strong solute-solvent coupling because of the change in charge distribution as model systems. An example of such reactions is the SN2 reaction of CH_3Cl and Cl^- in liquid - water. The solvation process in super critical water (SCW) is faster at liquid like densities but it becomes slower as the density decreases. The solvation compared in ambient liquid water, the overall solvation process in SCW at liquid like densities is an order of magnitude faster, but it becomes slower as density decreases. The solvent dynamics affects this by showing a bimodal behavior which involves a fast inertial regime lasting for a short time followed by a much slower diffusional regime that lasts for a long time.

3.5 Density Inhomogeneity Effects

Solvent density inhomogeneities determines the reaction environment which solute molecules in compressible fluids experience. They can also have an impact on the solvation effects such as hydrophobicity, solvent dynamics and referential solvation.

When a solute molecule is introduced into a solvent, it creates a local density perturbation due to the differences in solvent-solvent and solute-solvent interactions. This has an effect on the local solvent, and are accentuated at near critical conditions. At a critical point, the local solvent density around solute molecules can differ from the bulk solvent density.

The enhancement of the density occurs when water molecules are attracted to polarizable, polar or ionic solutes. If the solute-water interactions are weak, the extent of this density enhancement is reduced. This shows that local density inhomogeneity is a direct consequence of solute-solvent interactions.

Three density regions were observed for acetone and benzophenone in supercritical water (SCW).

-Strong density dependence at low densities$(\rho < \sim 0.5)$

-Weaker density dependence at high densities $(\rho < \sim 1.5)$

-Very little density dependence at near critical densities $(\sim 0.5 < \rho < \sim 1.5)$

Increasing the bulk density changes the local environment around the solute in the first region, it does not change the local density during the second region and it increases the local density in the third region.

The Kirkwood-buff fluctuation theory classifies mixture based on the nature of the solute-solvent interaction which determines the sign of potential molar volume. This theory also describes the local density in homogeneities around infinitely dilute solute molecules.

The classification of Kirkwood-buff fluctuation theory is based on the sign of the partial molar volume (VI) and the solute –solvent fluctuation integral.

$$Gij = \int_0^{\infty} (gij(r)^{-1} \, 4\pi r^2 \, dr \quad \textbf{(7)}$$

Where Gij is a solute-solvent pair correlation function

Mixture can be attractive, repulsive or weakly attractive.

Mixture is attractive if:

a. Partial molar volume (VI) is less than zero

b. Solute –solvent fluctuation integral (Gij) is greater than zero

Mixture is repulsive if:

c. Partial molar volume is greater than zero

d. Solute-solvent fluctuation integral is less than zero.

Mixture are weakly attractive if both the partial molar volume and the solute-solvent fluctuation integral are greater than zero.

3.6 Ions

Ions such as Na^+ and Cl^- are best studied to investigate the solvation of ions in water which is important for reactions that involve a change in charge distribution. It was observed from Na^+ and Cl^- those ion-water interactions are very strong and that the mixtures of ion-SCW are also strongly attractive. The water density in the first solvation shell is about an order of magnitude higher than the bulk density and similar to that observed for ion solutions at ambient conditions, which suggests that the local environment around these ions in SCW resembles that in the ambient liquid water. Result for the local and bulk water densities around a monovalent ion.

Studies done on divalent cations (Be^{2+}, Mg^{2+}), monovalent cations (Li^+, K^+) and anions (F^-, I^-) also agreed with the results of Na^+ and Cl^-.

In addition, the experimental measurement of redox potential for I_2/I^- reaction in SCW also showed that the ion –water interactions are very strong.

From these entire observations one can say that ion-water interactions in SCW are stronger than water–water interactions with ions disturbing the hydrogen-bonding structure of water. However, ion-ion interactions are stronger than ion –water interactions. This is because of the low dielectric constant of water at these conditions. The difference between cation-water and anion-water interactions is that the cation–water interaction are dominated by electrostatic interactions, whereas the anion-water interactions are primarily ion-water hydrogen bonding. Cations and anions exist as contact-ion pairs in SCW.

4. Organic Compounds

Organic compounds can be either repulsive or weakly attractive depending on how they interact with the surrounding water molecules. The interaction also depends on the functional groups of the organic compounds. For example, methanol and benzonitrile in SCW are weakly attractive near the critical point (T_r=1,05; ρ=1,0) whereas ,benzene and toluene are repulsive. This is because methanol and benzonitrile experience higher than -bulk- local water density, while benzene and toluene experience lower –than-bulk local water density. The opposite happens at a higher density (T_r=1,0; ρ=1, 5). Methanol and benzonitrile how experience lower –than bulk- local water density.

This explains that the nature of these organic compounds-water interactions changes with the bulk water density. At higher densities, methanol-water interactions are more repulsive in HTW, than in ambient liquid water. This Methanol (non polar solute) and water experience lower –than – bulk local water density. (Raymond Young 2000)

4.1.Role Of Density Inhomogeneity In Solvation Effects

Factors affecting the dielectric constant (Kw) of water are:

- **a.** Augmentation of water density around the solute molecules causes the dielectric constant of water to be higher than that of bulk water.
- **b.** Depletion of water density around the solute molecules causes the dielectric constant of water to be lower than that of bulk water.
- **c.** Change in local water density along the reaction path due to solute-solvent interactions cause changes in the dielectric constant.

d.Effect which local density in homogeneity has on the acid-catalyzed reactions in HTW causes the dielectric constant to be different than that of the bulk water.

Solvent density in homogeneity is an important factor to be included when performing certain chemical calculations. This is because of the accuracy of it. For example, accurate activation barriers are obtained for the SN_2 reaction of CH_3Cl and Cl^- and also hydrolysis solvent density in homogeneity also accurately describes how preferential solvations affect reactions in compressible HTW.

4.2 Physical Description Of The Model

The model presented in this work is developed for a reactor configuration where both the ground electrode (stainless steel, r=40 mm) and high voltage electrode (NiCr, r=2 mm, protrusion = 3 mm) are placed in a 1 L water solution with a gap distance of 5 cm .There are condition used in the experiments. The water conductivity was 150 $uscm^{-1}$ and the pH was 5.5 adjusted with KCl (1 Mm), and these values did not change throughout the experiment. A solution conductivity of 150 ums^{-1} gives a relatively dilute medium that has no observable effect on the bulk chemistry of the electrical discharge. it is also expected the relatively low concentration of chloride will not affect significantly the reactions that occur in the plasma region. (Fouad Zahran, Concepción Pando, Juan AR Renuncio, Albertina Cabaña,2012)

A set of test experiment with dilute containing HF, HCl, HI and HBr of the same conductivity to determine the effects of salt type on H_2O_2 was conducted for this study, and no effect of these species on H_2O_2 Formation was observed. On the other hand, the effect of these species (Cl^-,I^-,Br^-,F^-) on OH ,H_2 and O_2 formation is not known. There is possibility that chloride ions may lead to oxidation, but since the conductivity does not change over the course of the experiment, it was concluded that this effect is negligible. It can be observed experimentally that the streamers formed from the tip of high voltage electrode are approximately cylindrical in nature. For Mathematical simplicity and due to the approximate nature of mathematical model, the model presented here considers one half of an axially symmetric streamer in rectangular coordinates at the end of the lifetime of the core, all species in the core are placed in a lower temperature recombination region that has boundary with the bulk fluid. The recombination region is thus temporally coupled or coupled sequentially in time to the core. Other experimental evidence strongly suggests that a very high temperature is possible in a small volume. The voltage pulse has a very fast rise time on the order of 20 ns followed by approximately exponential decay.

The proposed discharge model follows the picture; the high temperature core is formed very rapidly during which the initiation reaction take place. A thermal energy balance was developed to account for the energy required to raise the temperature of the given number of moles of water found in the streamer channel to the boiling point, to vaporize and to the average temperature of the core and the recombination zones. The calculation are dominated by the energy required to heat the gas to the upper temperature limit. Recent heat capacity data for water gas between 100K and 600K was used .This calculation is simplified since it does not account for the effect of the temperature on the dissociation and the resulting differences in heat capacities of the gaseous mixture, the loss of heat by conduction or radiation heat consumed or produced by chemical reactions or other energy losses for mechanical effects eg. Shockwave formation. (Ray Marriott, Philip Jessop and Marie Barnes,2015)

Experimentally measurements provide only magnitude estimates of the streamer length and radius and these may vary substantially with different experimental conditions reported in the literature. There are not measurements of streamer length and diameter for the exact conditions for which we have measurements of H_2, H_2O_2, O_2 and OH. As mentioned above that the widths of the streamers in water have measured to be from 10 to 100 um. Setting the value of the core to 10 um radius is in the lower limit of this range. However, it is not clear from experimental results streamer widths if the observations of the visual regions correspond to a high temperature core and a cooler recombination zone.

In addition discharge may have some branching and may also vary in length, so the length value is also only in order of magnitude estimate.

It is therefore reasonable that given the known input energy 1 J and the order of magnitude estimates of the length and diameters, there is sufficient energy to raise this small volume of water to very high plasma temperature in a short period of time. More accurate measures of the stream radius and length and their time variations are certainly needed, particularly under the same conditions where chemical species are measured. The thermal energy and mass balances to determine temperature and concentrations with the model developed here are discussed separately in the following sections.

5.Model Formulation

5.1 Energy balance

The core is located in the centre of the discharge channel and it is assumed that the temperature at the centre of the core is 5000 K and the outer temperature is 2000 K. These temperatures are in the range of some experiments reported in the literature and they are lower than some reported modeling work that indicates temperature much higher, even up to 20.000 K. The temperature estimated in those previous models was calculated for a solution conductivity that is 6 orders of magnitude greater than that of the present case, and it is well known that the intensity of plasma channels strongly depends on the solution conductivity. However, it is likely that use of higher temperature may not have a strong effect on the results given here since most of the molecular species dissociated at temperature above 5000 K to 10.000 K. At the boundary of the core the temperature is 2000 K. The model structure proposed here incorporate the implicit assumption that hydrogen peroxide is formed in the recombination region and not in the core thus one measure of the distinction between the core and the recombination region is the formation of hydrogen peroxide.

The choice of the temperature cutoff between the high temperature core and the recombination region is somewhat arbitrary. (John L. Gohres, Alexander V. Popov, Rigoberto Hernandez, Charles L. Liotta and Charles A. Eckert 2009)

In reality there would be a more continuous change in the temperature with time and space. Further analysis is needed of both situation the time and spatial variation of the temperature. Without further knowledge of the full temperature profile in the plasma channel a reasonable starting point is to specify the starting point the boundary to occur in this temperature range .At the inner boundary of the recombination zone, temperature is 2000 K and the outer boundary it is 300K where the recombination zone meets the bulk solution.

5.2 The Core

The one dimensional thermal energy balance is given by**:**

$$\partial T/\partial t=\partial/\partial x(k(T)\partial T/\partial x) \quad \textbf{(8)}$$

Where k is the temperature dependent thermal conductivity .Thermal conductivity data as a function of the temperature were taken from that given by Matsunaga and Nagashima for the temperature range 300-2000K.The linear fit of the data of Matsunaga(r^2=0,998) gave the following equation:

$$K\ (WmK\text{-}) = 0,\ 00014T-0,035 \quad \textbf{(9)}$$

The above equation was taken to be the same for the core as for the recombination region because of its linearity and the fact that no data was available for thermal conductivity for the temperature range above 2000 K. Looking at the above equation which gives k=0.25 WmK^{-1}. This difference is relatively small that means k does not vary significantly with temperature over this range. It is highly possible that equation (9) is not quite accurate at temperature greater than 2000 K. For that reason the model result describing the temperature Profile for the core was tested with different arbitrary values ranging from 0.1 to 3 WmK^{-1} of thermal conductivity, but this variation had no effect on the overall concentration result. The core region mass balance are sequentially coupled to the recombination region in that result of the core model are in the input to the recombination region. However, the energy balance for and recombination region are only used to determine temperature profiles within each region and are not otherwise temporally coupled. Boundary and initial condition are given by:

X=0 T=5000 K

X=L T=2000 K ,L=10µm **(10)**

T=0 T=5000K

The recombination region in which the temperature profile is determined inside the core and the recombination region, the same thermal energy balance as well as the thermal conductivity equation for the recombination region was used Boundary and initial conditions for the recombination region are given by:

X=0 T=2000 K

X=L T=300 K ,L=200µm **(11)**

T=0 T=2000K

5.3 Results-Energy Balance

The model results for the temperature profiles inside the core and the recombination zone, respectively .The temperature profiles showing evolution with time were not included in the plot because of the final profiles shown how it formed much faster than the lifetimes of these two regions. It can be seen from the figure below. Its width and the time for its formation are much smaller than those of the recombination region .On the other hand the figure below shown that close to the edge of discharge channel $x=2x10^{-4}$ m where the channel meets the bulk fluid the decrease in the temperature.

5.4 Mass Balances

The species mass balance model is described first for the core and afterwards for the recombination region. The model results from the core were taken as the initial condition for the recombination region.

5.5 The Core Model.

The core is discharge zone where temperature at the centre is 5000 K and that at the boundary is 2000 K .The concentration profiles for the chosen species inside the streamer were obtained by solving the general material balance including chemical reaction and diffusion through the following equation:

$$\partial ci/\partial t = \partial/\partial x Di(T°)\partial ci/\partial x - \sum jRij \quad \textbf{(12)}$$

Where I indicates the species.

$D_i(T°)$ Is the temperature dependent diffusion

J represents the index for all reactions that involve species i.

R represents the elementary kinetics expression for each of the molecular and radical species considered in the model. The diffusion coefficient for all molecular and radical species is taken to be $D=10^{-2}m^2s^{-1}$ .This value was taken from the literature on available data for gas diffusion at the high temperature. Data were found for nitrogen diffusion at 5000 K and were used as an order of magnitude estimate for estimate for the diffusion coefficient of the species considered here at high temperature. It is assumed that the diffusion coefficient is not temperature dependent in the core primarily due to the lack of data for T>2000 K and due to the short time of existence (20 ns) and the small size of the region (10 µm). The following discussion supports the approximation that all species have the same order of magnitude diffusion coefficients, since the diffusion coefficients of radicals are unknown at elevated temperatures, the scaling procedure from radiation chemistry can be adopted:

$$\mathbf{D_i(T°)=D_{H2O}(T°)D_i(25°C)/D_{H2O}(25°C)}$$

Cherne: T denotes temperature.

Which can be easily calculated that the diffusion coefficient of hydrogen radical at any temperature is approximately three times greater than the diffusion coefficients of water at room temperature. The diffusion coefficients of all other species are similar to that of water at room temperature. The diffusion coefficient of all other species are similar to that of water. (Mizan ,T.I ;Savage, P.E; Ziff, R.M.J ,1996)

Table 4: In order to calculate $D_i(T°)$ one need to know $D_i(25°)$ as shown in the following table

i	SPECIES i	$D_i(25°C),(10^{-9}m^2s^{-1})$
1	H_2O	2.3
2	OH	2.2
3	H	7
4	H_2O_2	2.3
5	H_2	4.8
6	O_2	2.4
7	HO_2	2.3

Through calculations with this model it was found the result obtained for the core and recombination zones are not sensitive to changes in the diffusion coefficients of Hydrogen radical and molecular hydrogen so the assumption that all diffusion coefficients are equal to that of water is reasonable. The pressure in the discharge channel is the only adjustable parameter in the model, and it can be used with the assumed temperature to determine the initial concentration of water vapour. The initial concentration of water vapour in the core necessary to lead to the measured concentrations of molecular hydrogen, oxygen and hydrogen peroxide in the bulk was calculated to be 35 $molm^{-3}$ by adjusting the initial pressure values and using the ideal gas law:

$$C=p/RT \quad \textbf{(13)}$$

Knowing P=14 atm and T= 5000 K. Which gives c=35 mol m^{-3}.The results of model are very sensitive to the amount of water. This is a reasonable result because the initial concentrations of hydrogen and hydroxyl radicals depends strongly on the water vapour concentration.

It can be seen the core model assumes no hydrogen peroxide formation or HO_2 radical formation Thermo chemical calculation have shown that the bond dissociation energy (Kcal/mol of water follows this order:

H-OH (118.8)

H-O (102.4)

HO-OH (50.3) and

H-O_2 (47.2)

This would imply that at high temperature (2000 K – 5000 K) radicals such as HO_2 may dissociated. If any hydrogen peroxide is formed it would rapidly be thermally decomposed. The rate constant for hydrogen peroxide via OH radical recombination is assumed negligible at T>2000 K .The core model assumes that the only initiation reaction that takes place in the plasma is the following reaction:

$$H_2O+M \rightarrow H+OH+M$$

Where M= H_2O

This reaction is normally found in the dissociation of the water vapour and it is caused by the collision of water molecule yielding hydrogen and hydroxyl radicals. The same reaction products can be found in the radiation chemistry of liquid water where water molecules are split by high energy electrons (radiation) passing through the water according to the coming reaction:

Radiation

$$H_2O \rightarrow H+OH \quad E_{threshold}=5.1\ Ev \quad \textbf{(14)}$$

Where the H and OH radicals are involved in subsequent reactions listed in the table below. In modelling of the spur processes in water, radiation chemistry literature reports two additional initiation reactions:

Radiation H_2O

$$H_2O \rightarrow H_2+O(^1D) \rightarrow H_2+2OH \quad E_{threshold}=7Ev \quad \textbf{(15)}$$

Radiation

$H_2O \rightarrow 2H+O(^3P)$ Ethreshold=9.5 Ev **(16)**

Table 5: List of reaction used for the core model (M=H_2O)

nº	Reaction Nº	Reactions	Tº range (K)	Reaction order	Rate constant ($Cm^3molecule^{-1}s^{-1}$)
1	T2.1	H_2O+M---›H+OH+M	2000-6000	2	$5.8X10^{-9}exp^{(-440\ kjRT-1}$
2	T2.2	OH+M---›H+O+M	300-2500	2	$4.09X10^{-9}exp^{(-416\ kjRT-1}$
3	T2.3	O+H+M---›OH+M	1000-3000	3	$2X10^{-32}$
4	T2.4	H+H+M---›H_2+M	2500-7000	3	$1.68X10^{-32}$
5	T2.5	H_2+M---›H+H+M	2500-8000	2	$1.5X10^{-9}exp^{-402kjRt-1}$
6	T2.6	O+O+M---›O_2+M	300-5000	3	$9.26X10^{-34}(T/298)^{-1}$
7	T2.7	O_2+M---›O+O+M	2000-10000	2	$1.99X10^{-10}exp^{(-9,5kjRT-1)}$
8	T2.8	OH+O---›O_2+H	250-5000	2	$4.55X10^{-12}$ $(T/298)^{0.40}exp^{(49.64kjRT-1)}$
9	T2.9	OH+OH---›H_2O+O	250-3000	2	$1.02X10^{-12}$ $(T/298)^{1.40}exp^{(1.66kjRT-1)}$
10	T2.10	H+O_2---›O+OH	1000-5500	2	$2.56X10^{-11}$ $(T/298)^{0.55}exp^{(49.64kjRT-1)}$

Table 6: Initial and boundary conditions for the core (concentration of species in mol m^{-3}, L=10 µm, pulse duration=20 ns

nº	Species	t=0	x=0	x=L
1	OH	0	gradc=0	gradc=0
2	O_2	0	gradc=0	gradc=0
3	H_2	0	gradc=0	gradc=0
4	O	0	gradc=0	gradc=0
5	H	0	gradc=0	gradc=0
6	H_2O	80	gradc=0	gradc=0

Table 7: Average concentration of species in the core after 20ns

nº	Species	C (mol.m^{-3})
1	OH	14.1
2	O_2	0.11
3	H_2	0.61
4	O	0.3
5	H	14.1
6	H_2O	80

The reaction becomes an insignificant source of molecular hydrogen because the recombination of hydrogen radicals is now a much faster source .For the second mentioned above reaction is not utilized in the model. The table of initial and boundary conditions shows the initial and boundary conditions used in the model.

The average concentration in the core of each species after 20ns are determined using the trapezoidal rule integration and are shown in table above.

$$(c)Streamer = \int_0^L cdx = \int_0^L dx \quad \textbf{(17)}$$

Where c=Concentration at very x position (mol.m^{-3}) and L=width of the core region (m)

The figures below show the concentration profiles of molecular products and radicals in the core after 20ns.From what it appears that diffusion does not limit the reaction in the core but this mainly due to the short time of existence and small size of the region. The core model predict that molecular hydrogen is produced via recombination of H radical:

$$H+H+M \rightarrow H_2+M$$

From the result of the core model were the used as initial conditions for the recombination zone model as mentioned. The reaction by itself was sufficient to produce the correct concentrations of H_2 at the end of the pulse. Oxygen is produced in the core by the following reaction:

$$OH+OH \rightarrow H_2O+O \quad \textbf{(18)}$$

$$OH+O \rightarrow O_2+H \quad \textbf{(19)}$$

The oxygen concentration is low in the core due to the relatively low concentration of atoms present in the system. For this same reason, the combination reaction of oxygen atom to form O_2 is not significant here.

Literature from both combustion and ultrasonication indicate that molecular species can be present at these high temperature. It is also important to not that the effect of temperature on molecular dissociation is also strongly affected by pressure. Combustion literature data suggest that it is possible even at 5000 K to have significant quantities of undissocieted H_2, O_2 and H_2O at pressure in excess of 10 atm. More detailed analysis of plasma formed in ultrasound using the saha equation for plasma equilibrium indicate that only above 10000 K is most of the H_2O dissociated while some H_2 and O_2 are still present even at that temperature. Clearly below 5000 K molecular species can be present, particularly if the pressure is elevated as this model and work suggest (Xiaoyi Wang and Yulong Liao, 2018).

5.6 Recombination Region

Concentration profiles in the recombination region are determined using the following equation:

$$\partial ci/\partial t = \partial/\partial x Di(T^\circ)\partial ci/\partial x - \sum Rij \quad \textbf{(20)}$$

The data for diffusion coefficient as a function of temperature were taken from that given Matsunaga and Nagashima for the temperature range 300-2000 K. A cubic fit of that data of Matsunaga (R^2=0.999) gave the following expression:

$$\mathbf{D(m^2s^{-1})=-3x10^{-14}x\ T^3+3x10^{-10}x\ T^2-3.6x10^{-8}x\ T+1.5x10^{-6}\ (21)}$$

The model assumes no flux boundary conditions at the boundary with the bulk because it assumed that when the pulse is on, molecular species are formed in the streamer and none of them diffuse out into the bulk. The mixing of these species into the bulk solution takes place between pulses after the stremer disappears. This was justified by estimating how far a typical species can diffuse during one pulse. Assuming that the value of diffusion coefficient in liquids as

$10^{-9}m^2s^{-1}$ typically at 300 K the diffusion coefficient is in the range 10^{-8}-$10^{-11}m^2s^{-1}$ and the pulse duration of 10^{-6}s, it was estimated $x = \sqrt{Dt}$ **(22)**

That a typical species can diffuse 0.03 μm at the temperature near the boundary of the discharge channel, thereby justifying the no-flux condition of the boundary of the recombination zone with the bulk fluid where the temperature is approximately 300 K. This result is in contrast to the high rates of diffusion within the main regions of both the core and recombination zone where the temperature are much higher.

No-flux conditions for each species are also used at x=0 for symmetry since for the majority of the lifetime of the recombination region the core is not in existence. The core provides the seed for the recombination region through determination of the initial conditions. The core and the recombination region are thus coupled sequentially in time. This discrete representation of the time and spatial variation is only an approximation and future modelling efforts can consider the continous variation in time and space of species and temperature.

6. Discussion

The model values of the rate of species production per second were compared with the experimental value reported in the table below

Table 7: Comparison between calculated and measured production rates of each species after 1 s of experiment rates (Ms^{-1})

nº	Species	Model	Experiment
1	H_2O_2	$6.9x10^{-7}$	$6.9x10^{-7}$
2	H_2	$11x10^{-7}$	$11.9x10^{-7}$
3	O_2	$2.6x10^{-7}$	$2.4x10^{-7}$
4	OH	$9.7x10^{-7}$	$6.7x10^{-8}$
5	O_2^-	$1.1x10^{-8}$	$6x10^{-8}$

Table 8: Comparison between calculated and measured average bulk concentration of each species after 1 h experiment. C (Mm)

nº	Species	Model	Experiment
1	H_2O_2	2.4	2
2	H_2	3.9	4
3	O_2	0.93	1
4	OH	0.0349	0.036

The model output for the OH radical concentration was not fit to the model, and thus the good agreement provides support for the validity of the model. The radical O_2^- is formed by the equilibrium reaction

$$HO_2 \rightarrow O_2^- + H^+ \quad \textbf{(23)}$$

with pKa=4.8 at ambient conditions. The model value was determined from the HO_2 molar rate of production ($2.3x10^{-9}$ Ms^{-1}). Using pH 5.5 and these equilibrium relationships. The agreement is acceptable. However, further information on the value of pKa at high temperatures is needed for more accurate analysis. Regarding the molecular species formation mechanism, several observations were made. Analysis of the recombination region model confirms that the recombination of hydroxyl radicals is the major pathway to hydrogen peroxide formation according to the following equation:

$$OH+OH \rightarrow H_2O_2 \quad \textbf{(24)}$$

Regarding the oxygen formation, the model predicts that two pathways are linked to oxygen formation and both depend on the initial hydroxyl radical formation:

Pathway 1: $OH+O \rightarrow O_2+H_2$ **(25)**

Pathway 2:

$OH+OH \rightarrow H_2O_2$ **(26)**

$H_2O_2+OH \rightarrow HO_2+H_2O$ **(27)**

$HO_2+OH \rightarrow H_2O+ O_2$ **(28)**

In the oxygen formation, it should be mentioned that 47 % of the molecular oxygen is formed in the core as described which can takes place in the high temperature core as well as in the recombination region, is a precursor to oxygen formation. In the recombination region, by setting the reaction rate constant of reaction to zero and leaving the reaction. It was found that reaction in pathway 1 contributes approximately 20 % to the total oxygen concentration found at the end of the pulse.

The contribution of pathway 2 to the total oxygen concentration is 33 % which was determined by setting the reaction rate constant of reaction to zero. This percentage was obtained from ratio of the oxygen concentration.

Pathway1 is supported by the work of Kaufman and Del Greco where the gas phase discharge of water vapour is studied and the same reaction for the oxygen formation was reported. Pathway 2 is supported by the work of Sahni where one of the possible pathway for oxygen formation is the same as presented here in pathway 2. Kirkpatrick claimed that pathway 2 is not a possible route for oxygen formation. He performed an experimental where the solution was charged with initial concentration of 2 Mm hydrogen peroxide.

His hypothesis was that if hydrogen peroxide decomposition was the major source for oxygen production, the oxygen concentration measured in this experiment would have been higher than that seen without hydrogen peroxide.

His experiment results revealed that the oxygen production and the rate of production of hydrogen peroxide are very similar in the two experiments with or without oxygen peroxide addition. As it show in the work of Sahni et al it is very important for the scavenger to have a high volatility and high concentration in order to exist in significant concentration in a streamer.

It is well known that the vapour pressure of H_2O_2 is very low; therefore one can assume that none of the initially placed H_2O_2 in the reactor by Kirkpatrick entered the streamer. This was a further confirmation by analyzing the data for hydrogen peroxide. Concentration where the initial concentration of 2 mM added to the amount produced by discharge 2 Mm was equal to 4 Mm at the end of experiment. The majority of hydrogen is formed in the core at high temperature via recombination of hydrogen atom .It was calculated that in the recombination region the reaction that contributes 21 % of total hydrogen concentration found at the end of the pulse is

$H+OH \rightarrow O+H_2$ **(29)**

Also the reaction in which hydrogen atom recombine to form molecular hydrogen contributes insignificantly in this region. (Keith J Laidler, John H.Meiser, 2005)

7. Concluding Remarks

HTW is a very unique medium for organic chemical reactions. It was defined as liquid water at about 200 °C and supercritical water up to 600 °C. The properties of HTW within the above boundaries vary with pressure and temperature. At the two boundaries water can be considered as a hot, expanded liquid and as well as a nearly ideal, high-temperature gas. Effects that are considered important in other supercritical fluids can also be important for HTW near its critical points. The critical point of water (Tc=374◦C, Pc=218 Atm).

Water can also participate in hydrogen-bonding interaction and this is one of the unique feature of chemical reaction kinetics in HTW. Several factors arise when water participates in hydrogen-bonding interaction.

a) formation of lower-energy transition states is allowed
b) Already existing transition states can also be stabilized and this will dissociate to form H^+ and OH^-

The H^+ and OH^- will in turn accelerate acid-catalyzed and base catalyzed reactions. The roles of water are summarized in the table 3 below that have been highlighted this review. I have attempted to provide this information in such a form that reader can identify the roles and effects of water that likely to be important for a particular chemistry at particular set of reaction conditions.

For the first time a model can be developed to described the primary reactions taking place in electrical discharge in water during and in one pulse. The model assumes that the discharge channel is composed of two sequentially coupled zone:

The core and recombination region. The core temperature varies with the position from 5000 K at the centre to 2000 K at the boundary (10 µm).The temperature in the recombination region is 2000 K at the centre and 300 K at the boundary with the bulk (200 µm).

The thermal energy balance and the species mass balance were solved for both zones. Based on the set of reactions considered, the model predicts that of all the molecular hydrogen found at the end of the pulse, 79 % is formed in the core at high temperature, 21 % is formed in the recombination region and that the main reaction for hydrogen formation is the recombination of hydrogen atoms. Hydrogen peroxide is formed in the recombination region via recombination of hydroxyl radicals. In the core 47 % of the oxygen is formed by reactions between oxygen radicals and hydroxyl radicals and the source of oxygen radicals is the recombination of hydroxyl radicals.

8. General Recommendation

Due to the very low concentration of oxygen radicals, the recombination of oxygen radicals is not the major pathway for molecular oxygen formation as in the case of of hydrogen.

For this the one adjustable parameter in the system is the concentration of water vapour (35 mol m^{-3}) which can be used to estimate the pressure (14 atm). The model simulates the experimentally measured value of molecular hydrogen, oxygen, hydrogen peroxide and hydroxyl radicals very closely. The physical structure of the model can be improved with further understanding of the temperature and pressure time and spatial distributions in the discharge channel. Further knowledge of the effects of these conditions on the chemical reactions can lead to more complete description. However the model developed in this work provides a basis and starting point for more analysis of this important and interesting topic. Information technologies challenge us to re-examine what is possible to learn, because they can bring new resources and approaches into teaching that are not conceivable without technology. For instance, it is possible for nine years olds to interpret graphs they generate through interactions with sensors. Eleven years olds can gain intuitive understanding of basics calculus concepts by using a position sensor with a computer that generates real-time graph of the students motion and velocity .Genetics can be learned through interactive simulations. The nature of chemical bonds can be understood through real-time orbitals visualized in 3D.

The role of water that have been highlighted throughout this work. I have try to attempt to provide this information in such form that readers can identify the role and effect of water that likely to important.

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