γ- RADIOLYTIC GENERATION OF POLYSULPHIDE FROM AQUEOUS SODIUM SULPHIDE SOLUTIONS

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by

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ABSTRACT

The mechanism of polysulphide formation by γ -radiation of aqueous sodium sulphide (Na₂S) solutions was investigated. The roles of solvated electron (\bar{e}_{aq}) and hydroxyl radicals (\cdot OH), as primary products of water radiolysis, were studied in a systematic manner by using N₂O as \bar{e}_{aq} and 2-propanol as \cdot OH scavengers. Polysulphide formation in Na₂S solutions was found to be initiated by the oxidizing intermediate, the \cdot OH radical.

The scavenger experiments were supplemented by other studies on effects of solute concentration, dose at a single dose rate, pH, oxygen and hydrogen sulphide (H₂S) saturation.

Rates of polysulphide formation increased according to presence of N_2O and H_2S , Na_2S concentration, irradiation dose and were highest at pH 7.0.

In these experiments, highest polysulphide yield, 14 g/l, was obtained in the 80 g/l aq Na_2S-H_2S system at pH 12.7 and exposed for 20 Mrad dosage.

The effect of oxygen was to increase radiation yield for lower dose ranges. At higher doses, however, G-values fluctuated markedly.

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LIST OF SYMBOLS

A _x	Group IV, V and VI elements in the periodic table.
Br	Bromide ion.
•Br	Bromine radical.
c1 ⁻	Chloride ion.
·Cl	Chlorine radical.
E	Redox potential.
Ē	Electron.
e aq	Solvated (hydrated) electron.
e therm	Thermalized electron.
F	Faraday in appropriate unit.
G _{ē + •} ∺	Radiation yield as sum of primary reducing species.
с _м	Radiation yield of molecules.
G _P	Radiation yield of final products.
G _R	Radiation yield of radical species.
G (X)	Radiation yield of measured total X (atoms, radicals or molecules) produced in and out of spurs of a given reaction.
с _х	Radiation yield of X produced only in spurs.
н+	Hydrogen ion.
Н	Hydride ion.
HO2	Perhydroxy ion.
• HO 2	Perhydroxy radical.
H2 ⁺	Acidic form of hydrogen molecule ion.

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- •H Hydrogen radical.
- H₂ Hydrogen molecule.

 H_2O^{T} Positive parent ion in water radiolysis.

- H₂O^{*} Excited water molecule.
- H₂O₂ Hydrogen peroxide.

H₃O⁺ Hydrated proton (acidic hydrogen).

HS Hydrogen sulphide ion.

•HSO, Hydroxosulphuroxy radical.

^K·R+ ϕ Reaction rate constant between radical species (·R) and scavenger concentration (ϕ).

LET Linear energy transfer (kev/M). This is defined as the linear-rate energy loss (locally absorbed) by an ionizing particle traversing a material medium.

M Molecule in general.

Mrad Unit of radiation dose (10⁶ rad).

O Monoöxygen (-I),

- OH Hydroxide ion.
- •OH Hydroxyl radical.
- 0₂ Oxygen molecule.

0, Hyperoxide.

0, Ozonide ion.

0 Oxyanion in general.

P Product.

Q Substance reacted.

R Gas constant.

R H or alkyl group.

•R Radical species.

Spur Small cluster when referring to small groups of excited and ionized species.

So Elemental sulphur.

•S Sulphur radical.

S* Labelled sulphur atom.

S Sulphide ion.

SO₂ Sulphite ion.

SO _____ Sulphate ion.

X

S₂O₃ Thiosulphate ion.

S_nS⁻ Polysulphide excess sulphur.

Track Path by which protons or particles in radiation chemistry can ionize or excite a large number of molecules.

Ratio between polysulphide excess sulphur and sulphide sulphur.

In loving memory of my mother,

DORRAE YOU (1904 - 1968)

and my brother,

BONG - SOO YOU (1922 - 1966).

1.0. INTRODUCTION

In recent years, much pulping research has been aimed at modifying existing processes or finding new ones additional to those already practiced. The improvements sought are in the area of higher pulp yield and/or qualities. Further improvements are desirable with respect to ease and extent of spent chemical recovery and reduced impact on environmental quality. One attractive process appears to reside in the rediscovered effects of polysulphide in alkaline pulping liquors. Polysulphide pulping, as a modification of kraft pulping by addition or generation of sodium polysulphide, is one of the few potential methods by which increased yield and changes in kraft pulp properties can be obtained economically.

During recent years several modifications to the kraft or alkaline cooking processes have been proposed. Some additives, such as dithionite (52 to 55), sodium borohydride (63) and hydrazine (71) are only of theoretical interest due to higher production costs with their use, as compared to the conventional kraft cook (95). One of the oldest suggestions, cooking with liquor containing polysulphide, seems to be more attractive. Thus, new attention has been focussed by different researchers on revival of polysulphide cooking.

Changes observable in pulp quality, when pulping with polysulphide liquors, depend upon the amount of excess sulphur used in cooking. With 4% excess sulphur, for example, approximately 10% reduction in wood consumption is experienced and

pulp characteristics are changed rather drastically. First of all, the pulp is beaten more easily. The effect is believed to result from an increase in retained hemicelluloses. The resultant paper, however, has lower tear resistance, which is one of the main drawbacks of polysulphide pulps (41). From the point of response to beating, and stock freeness, polysulphide pulps seem to be a very attractive alternative to conventional kraft pulps, but where tear is an important strength consideration polysulphide cooking is less favored.

During black liquor recirculation in the kraft recovery process, the viscous black liquor contains less than 100% of the original inorganic elements present in the initial white liquor. This is partly due to the fact that the pulp cannot be washed completely free of inorganic ions. Therefore, makeup chemical is added in an amount equivalent to these losses (59). The decrease of chemical concentration in recirculated polysulphide cooking liquors also falls into this category. While cooking liquor makeup involves only addition of elemental sulfur to the white liquor, polysulphide stabilization, especially at high (cooking) temperatures, appears to be exceedingly difficult. Much work has been done in attempts to prevent chemical losses from polysulphide alkaline pulping liquors (64).

No studies have been reported previously which involve radiolytic generation of polysulphide.

The general scheme of radiation chemical investigations may be represented as follows (73):



Previous studies in these laboratories have shown that polysulphide can be formed from aqueous sodium sulphide by γ -radiation (23, 99). The radiation yield (G-value) was about 1.0 in a system containing 80 g/l Na₂S under 270 psi H₂S and exposed for 70.8 Mrad. The mechanism of polysulphide formation and effects of dosage, pH, oxygen, H₂S and X_s-values were not clear.

The objectives of the present work were:

- (i) to study the role of two radical species, \bar{e}_{aq} and $\cdot OH$, formed from water radiolysis in polysulphide generation; and
- (ii) to examine some parameters, such as solute concentration, additives and initial pH, which may relate to polysulphide yield by radiolysis.

The role of \overline{e}_{aq} and $\cdot OH$ on mechanism of polysulphide formation was studied by using radical scavengers. Nitrous oxide was used as an electron scavenger and 2-propanol as the $\cdot OH$ radical scavenger.

2.0. LITERATURE SURVEY

2.1. Polysulphide

A review of literature pertinent to the present study divides as: pulping characteristics, solution preparations and associated analytical techniques.

2.1.1. Pulping with polysulphide liquors

In 1946 Hägglund (38) first noted an increase in pulp yield after direct sulphur addition to caustic pulping liquors. Subsequently, numerous studies have reported on the nature of yield increase with different woods (41, 85), mechanism of polysulphide pulping (10, 66, 67, 85) and characterization of polysulphide pulps (9, 10, 12, 22, 25, 37, 66, 67, 85). In the last few years attention has been given to optimization of yield increase, as exemplified by the work of Teder and coworkers (9, 37, 88, 90, 92, 93) and Clayton and Sakai (24, 25).

Commercial adaptation of the polysulphide process has been announced by only one mill. The Norwegian kraft mill, Lovenskiold-Vaekero, Hurum Fabriker, converted to polysulphide pulping in October 1967 (47). This mill reported a 3.5 to 4.0% yield increase by addition of 2.2% elemental sulphur. Assuming constant sulphidity, this means that sulphur losses must be in the neighbourhood of 90 lb/ton of pulp (oven-dry basis). Herein is a major reason why the polysulphide process has not replaced conventional kraft pulping; without a recovery process for the added sulphur, losses are extremely high and these occur mainly as objectionable pollutants. Another factor which

might be a drawback is increased sulphidity resulting from direct sulphur addition.

Dissolution of polymer molecules, physical rearrangements resulting in increased odor, degradation through 'peelingoff', alkaline hydrolysis of glucosidic bonds, and redeposition of polymer molecules, are reactions occurring during polysulphide cooking (41). Polysulphide can oxidize terminal aldose groups on wood polysacharides to aldonic acids, which then can not rearrange to form ketoses. Alkaline peeling can then begin only at end-groups which have escaped oxidation, or at endgroups created by alkaline hydrolysis (24). The increase in yield appears to result from oxidation of polysaccharide reducing end-groups to acids which provides resistance to 'peelingoff' degradation in hot alkali. With polysulphide pulping the yield of all wood carbohydrates increases, particularly glucomannan in coniferous woods and glucuronoxylans in pored woods (10, 85, 95).

Polysulphide also reacts with wood lignins. Evidence that the polysulphide ion might react with lignin was given by Nakano <u>et al</u>. (67), who experimented with lignin model compounds. They found that when vanillyl alcohol and apocynol were treated with polysulphide liquor the reactions yielded much more vanillin and acetoguaiacone, respectively, than after similar treatment with kraft liquor. The higher yield of vanillin might have been due to oxidation via vanillyl disulphide, since this intermediate compound was isolated after polysulphide treatment (66), but not after treatment with kraft liquor.

The rate of delignification in polysulphide pulping is considerably faster than in the kraft process. Resulting coniferous wood pulps are comparable to kraft in all strength properties, with the possible exception of tear (24, 85, 88). The presence of lignin decreases stability of polysulphide solutions. Although initial lignin-polysulphide reactions might lead to consumption of polysulphide in wood pulping, this effect is smaller than thermal degradation of polysulphide solutions. The resulting lignin modification could possibly make it more easily removed during subsequent stages of the pulping process (88). The color of polysulphide pulp is usually darker than that of comparable kraft, thus requiring stronger bleaching treatments.

In order to optimize pulp yield and quality, two stage or multistage polysulphide alkali cooks have been proposed (24, 51). Aqueous calcium polysulphide solutions are known to be more effective in stabilizing carbohydrates toward alkaline degradation than corresponding aqueous sodium polysulphide solutions (87). The considerable additional carbohydrate stabilization obtained in the presence of calcium ions originates only to a minor extent from accelerated metasaccharinic acid end-group formation. It mainly results from extensive and rapid oxidation of carbonyl end-groups to mannoic acid.

2.1.2. Polysulphide solution characteristics

The composition of aqueous sodium polysulphide solutions includes various polysulphide ions, S_nS^- , as well as HS⁻, S⁻ and OH⁻ ions (93). The effect of S⁻, OH⁻ and X_S (the ratio

between polysulphide excess sulphur and sulphide sulphur) is similar, irrespective of whether calcium or sodium is used as the cation (87).

Several workers have investigated equilibria in aqueous solutions at room temperature between S_nS^- of different chain lengths and HS⁻, S⁻ and OH⁻. Rapid acidimetric titration and redox potential measurements have been used (26, 62, 85). Cloke (26) indicated in 1963 that the mean polysulphide ion is larger than the stoichiometric composition, i.e., that considerable amounts of HS⁻ or S⁻ exist in solution. All equilibrium studies indicate that S_3S^- and S_4S^- ions are the dominant species. Single protonated polysulphide ions seem to be unstable as polysulphide solutions decompose into HS⁻ and S_0 when they are slowly acidified to pH values below 9 (35).

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Teder (89) postulated that even if it were impossible to prepare polysulphide ions larger than S_4S^{--} the possibility could not be neglected, since, for instance, S_4S^{--} and larger ions could be in equilibrium with smaller ions than S_4S^{--} in the stoichiometric composition. This contradicts previous studies on polysulphide equilibria.

Ames and Willard (12), Rodziewicz <u>et al</u>. (82) and Voge and Libby (96) have reported that all sulphur atoms, upon formation of thiosalts and di- and polysulphides, are interchangeable with each other, as:

It is known that aqueous polysulphide solutions have a stable redox potential that varies with composition at room temperature and at comparatively low alkalinities (26). According to Teder (90), the redox potential of polysulphide solutions at given temperature is dependent on the X_s value, excess sulfur concentration (S_0) and OH⁻. The ability of polysulphide solution to stabilize carbohydrates can be predicted from the redox potential (E), by:

$$E + \frac{RT}{F} \left[\frac{3}{2} \cdot \ln[OH^{-}] + \ln[S_{O}] \right] \dots [2-3]$$

where:

E = electromotive force (emf), volts; R = gas constant, 0.08206 l.atm deg⁻¹.mole⁻¹; T = absolute temperature, ^OK; and F = faraday in appropriate units, 96,487 coulombs/ eq. = 23,060 cal/volt - eq.

If the above sum is below a certain value (-725 mv at 90^oC) no stabilization is obtained. Above this limit the ability of polysulphide solutions to stabilize hydrocellulose and carbohydrates in wood seems to be an approximately linear function of the above variables at a given temperature.

The kinetics of polysulphide rearrangement reactions were studied by spectrophotometric methods (92). In aqueous solutions of Na₂S, the different polysulphide ions are in equilibrium with HS⁻ and OH⁻:

$$s_{(m+n)}s^{-} + Hs^{-} + OH^{-} \xrightarrow{\qquad} s_ms^{-} + s_ns^{-} + H_2O$$
 ..[2-4]

The equilibria were disturbed by addition of OH^- or HS^- . Rate of rearrangement was found to increase with increased S_0 , ionic strength, and temperature, and decrease with decreased $OH^$ and X_S level. Rearrangement reactions occurring in polysulphide solutions are thought to be considerably faster than reactions with organic compounds or that of thermal polysulphide decomposition.

The thermal decomposition of sodium polysulphide has been studied in alkaline aqueous solutions (24, 37, 75). Unwanted polysulphide losses can occur while polysulphide pulping liquor is being prepared, causticized or stored at elevated temperatures (70 to 130° C). Polysulphide ions decompose into thiosulfate and hydrogen sulphide ions, as:

 $s_n s^{--} + (n-1)OH^- + (1-\frac{n}{4})H_2O \longrightarrow (1+\frac{n}{2})Hs^- + \frac{n}{4}s_2O_3^{--} \dots [2-5]$

According to Olsson and Samuelson (75), and Teder (88), this decomposition is accelerated by increased temperature, alkalinity and X_s .

Thermal polysulphide decomposition is known to occur as a result of alkaline degradation of polysulphide ions. This is independent of both acid decomposition of polysulphide into S_0 and HS⁻ ions, and oxidation of polysulphide with molecular oxygen to $S_2 O_3^{--}$ (24, 75).

The mechanism of polysulphide ion alkaline degradation can be drawn from the alkali induced scission of the S-S bond in organic disulfides. When hydrogen is not split off from

the organic groups, the initial reaction is believed to be:

$$R' - S - S - R' + OH^{-} \xrightarrow{RS - OH + RS^{-} \dots [2-6]}$$

Whether a polysulphide solution is stable or not at a given temperature is determined by HS⁻ and OH⁻ concentrations, whereas $S_2O_3^{--}$ concentration has no observable influence (37). Since the stabilizing effect of HS⁻ is considerably larger than the counteracting effect of OH⁻, concentrated polysulphide solutions are as a rule more stable than dilute ones. Decomposition of polysulphide solutions having low stability seems to start with a nucleophilic attack of OH⁻ on the polysulphide ion. This reaction is probably rate determining.

Activation energy is lower for solutions containing larger polysulphide ions than for solutions with smaller mean polysulphide ion size (37).

2.1.3. Polysulphide solution preparations

n = 2, the reaction is fast

Early investigations on polysulphide seem to have originated with Bloxam in 1895 and 1900 (78). He found that S_0 dissolves in aqueous S⁻⁻ solutions forming S_nS^{--} and $S_2O_3^{--}$ and that formation of the latter is depressed by decreased alkalinity. It had been known that the dissolving rate of S_0 was faster in S_nS^{--} than in S⁻⁻ solution (21), as:

when:

n = 3, the reaction is slow,

n = 4 or n = 0, the reaction is slowest.

The simplest and most common way to prepare aqueous polysulphide solutions for laboratory or commercial pulping purposes is to dissolve S_0 in aqueous alkaline sulphide solutions. For example, white liquor or recycled liquor from the first stage of a multistage pulping process may be treated. The S_0 can be produced by any of the procedures proposed for chemical recovery (20, 56), or it can be a "make-up" chemical.

The rate of S_0 dissolution in aqueous Na_2S at various alkalinities has been studied (42) and is known to be approximately proportional to specific surface of the S_0 . Mass transfer in the liquid is of minor importance, as long as all particles are in contact over their entire surface with the liquor. In this, sulphide ions seem to follow a second order reaction at moderate rate. Polysulphide ions, possibly in combination with S^{--} , react at a high rate according to a mixed first order reaction. Although the former reaction has a fairly low activation energy, the latter exhibits even lower value. Experimental evidence suggests that small polysulphide ions are more active but less stable than larger ones.

The possibility of making polysulphide at elevated temperature by processing sodium-sulphur compounds available in the kraft recovery system (Na_2SO_4 , Na_2S , $Na_2S_2O_3$) has not been considered previously. It is known, however, that there are three possibilities for formation of polysulphides from

these compounds (8), namely:

(i) thermal decomposition of $S_2 O_3^{--}$;

- (ii) partial reduction of SO_A^{--} ; and
- (iii) partial oxidation of S⁻ in the absence of water, at atmospheric pressure and with restricted air contact.

2.1.4. Polysulphide solution (fresh/used) analyses

In early stages of polysulphide analytical investigations, Ahlgren and Hartler (6) determined polysulphide excess sulphur by the copper column method. This was modified by Bilberg and Landmark (18) who employed copper metal to isolate polysulphide, which was then reduced and analyzed. This method gives polysulphide values higher than those obtained by other analytical techniques.

Olsson and Samuelson (74) developed an ion exchange procedure for S_nS^- , S^- and $S_2O_3^-$ determination in black liquors. Teder (88), however, chose the Bilberg - Landmark method in preference to ion exchange. The present TAPPI method (T 624 - OS 68) is intended primarily for kraft liquors in which SO_3^- concentration is low. It is not reliable for analyzing alkaline liquors containing large amounts of SO_3^- , due to partial coprecipitation of zinc sulphite with the zinc sulphide during the zinc carbonate metathesis step. Modification of this well-known volumetric standard method for the determination of S^- , $S_2O_3^-$ and SO_3^- or S_nS^- has been investigated (81).

In 1967, Ahlgren (5) examined an acidimetric method for determining S^{--} sulphur and S_0 . The advantage of

this procedure, by comparison with other methods known for analyzing polysulphide liquors, is the possibility of determining in a single operation all sulphur components of interest to pulping. It should be pointed out, however, that for each single component in the liquor other methods may exist which are more precise than acidimetric titration (6).

It is known that aqueous polysulphide solutions have a stable redox potential that varies with composition (26, 62, 78). Methods for determining excess sulphur in polysulphide solutions, based on redox titration, have been investigated (7, 77, 90). Redox potentials for polysulphide solutions, within wide ranges of X_s , S_o and OH⁻ concentration were determined. The redox potential of a polysulphide solution at a given temperature is dependent on all of these (90).

Recently, spectrophotometric studies on polysulphide solutions have been carried out by Teder (89, 91, 94). Difficulties in obtaining stable spectra from polysulphide solutions have been reported (26). The spectroscopic method is based on measurement of sample absorbance at 285 nm in thin silica cells after dilution with slightly alkaline NaCl solution. At this wave-length, aqueous Na₂S_nS solutions of different types have almost the same absorptivity based on excess sulphur. The spectroscopic method has been compared with other methods and is generally found to be equally accurate, but more rapid. For determining differences in excess sulphur concentration within a series of polysulphide solutions of the same type, the spectroscopic technique is considerably more accurate than other known methods (89).

2.2. Radiolytic Processes in Aqueous Environment

Polysulphide formation by irradiation of aqueous Na₂S solutions has not been reported in the literature previously. Radiation chemistry of water, however, has been much explored.

In order to probe radiolysis mechanisms of aqueous solutions, it is necessary to understand the radiolysis of water. Since water is the main component of environment in dilute aqueous systems, it initially absorbs almost all the radiation energy. Relatively little radiation energy is absorbed directly by the solute, but the solute may be affected indirectly. By absorbing most of the radiation energy, the solvent produces reactive species and reaction between these and solutes may then occur.

2.2.1. Ionized and excited species

Gamma-radiation of water produces ionized and excited species. The ionization process is believed to be of much greater importance to chemical changes than the excitation processes in liquid water. The ionization process may be represented (86), as:

 $H_2O \xrightarrow{\gamma} H_2O^+ + \overline{e}$ [2-8]

A considerable part of the total energy absorbed from high-energy radiation (10 to 15%) is dissipated by sub-excitation of electrons which ultimately end as thermalized electrons

 (\bar{e}_{therm}) . There is a close relationship between the formation of primary radical products in water and the fate of sub-excitation and \bar{e}_{therm} (33).

Samuel and Magee (84) calculated that the time required for an electron to return to the parent ion from a distance varying between 5 and 100 Å ranges from 10^{-15} to 10^{-11} sec. The thermalizing process takes about 10^{-13} sec. Due to electrostatic attraction, the electron would be drawn back to the positive parent ion (H_20^+) , thereby neutralizing it and producing a highly excited water molecule, H_20^* , such as:

$$H_2O^+ + \bar{e} \longrightarrow H_2O^* \dots [2-9]$$

This excited molecule may further dissociate into a hydrogen radical (\cdot H) and a hydroxyl radical (\cdot OH), according to:

The •H and •OH radicals are formed with sufficient energy to diffuse from the solvent cage.

Concerning the fate of H_2O^+ formed in the primary ionization [2-8], it is highly probable that this species reacts with another water molecule before it is neutralized by the electron (57):

 $H_2O^+ + H_2O \longrightarrow H_3O^+ + \cdot OH \dots [2-11]$

When H_30^+ is neutralized by recapture of an electron, the unstable, partially solvated entity, H_3^-0 , is produced. This can undergo two thermal dissociation reactions, as:

$$H_30^+ + \bar{e} \longrightarrow H_30 \longrightarrow H_20 + \cdot H \ldots [2-12]$$

 $H_{3}^{0} \iff H_{3}^{0}^{+} + \bar{e}_{aq} \longrightarrow H_{2}^{0} + \cdot H \dots [2-13]$

where:

 \bar{e}_{aq} represents the solvated electron; i.e., $\bar{e}_{aq} = H_2 O^- = (H_2 O)^-$.

The net outcome of either [2-10] or [2-11] and [2-12] is production of the same products, \cdot H and \cdot OH radicals.

According to Gray (36) and Lea (58), the secondary electron would travel approximately 150 Å from the H_2O^+ before its energy is thermalized. They postulated that the \cdot OH radical is produced near the track of the secondary electron by [2-11]. With regard to the secondary electron, which is free of electrostatic attraction from H_2O^+ and away from the track, they suggested that it produces \cdot H atoms on reaction with H_2O molecules, as:

 $H_2O + \bar{e} \longrightarrow OH + H \dots [2-14]$

Further, •H reacts with any solute present.

Platzman (79) considered energy loss by secondary

electrons and estimated that a 10 eV electron would travel approximately 50 Å away from its parent ion before its energy is thermalized. At such a distance the electron would not be influenced by the electrostatic field of the parent ion. Thermal equilibrium between \bar{e}_{therm} and water was established and the reaction was found to be relatively slow (approximately 10^{-11} sec). From this point of view, it was concluded that electrons ejected in the water ionization process become thermalized and hydrated:

$$\bar{e} \longrightarrow \bar{e}_{therm} \longrightarrow \bar{e}_{aq} \dots [2-15]$$

Both the Samuel-Magee and Lea-Gray-Platzman models are presently accepted as describing processes occurring in irradiated aqueous systems.

In spurs, where initial radical concentration is high, the following recombination reactions (86) are possible:

The hydrogen gas and hydrogen peroxide are molecular products, whereas the \cdot H, \bar{e}_{aq} and \cdot OH formed [2-10 to 2-15] are radical products.

Radiation-induced water decomposition can be summarized

as:

$$H_2^0 \xrightarrow{\gamma} H_3^{0_{aq}^+}, \cdot OH, \overline{e}_{aq}, \cdot H, H_2^{0}, H_2^{0}, \dots [2-20]$$

Of these species, the role of \cdot OH radicals and solvated electrons, \overline{e}_{aq} , are the most important in radiation chemical reactions. G-values of water radiolysis products have been shown (97) to be:

$$G_{(e_{aq})} = 2.7$$
 $G_{(\cdot OH)} = 2.75$
 $G_{(\cdot H)} = 0.55$ $G_{(OH^-)} = 0.1$
 $G_{(H_3O^+)} = 2.8$ $G_{(H_2O_2)} = 0.7$
 $G_{(H_2)} = 0.45$

The formation of these products in irradiated water is independent of type and energy of radiation. Radiation yields (G-values), depend on effects of linear energy transfer (LET) from radiation and upon other parameters, such as scavenger reactivity, pH, oxygen and dose rate (33).

The hydroxyl radical, \cdot OH, and its dimer H₂O₂ are the main, and practically only oxidizing primary products of water radiolysis. Reducing species among primary products are the \bar{e}_{aq} and \cdot H also present in irradiated water (33). Since \bar{e}_{aq}

and \cdot OH play important roles in aqueous systems (33), only these two are discussed further.

2.2.2. Solvated electrons (eag)

The symbol, \bar{e}_{aq} , is used to represent the solvated (hydrated) electron, although H_2^0 or (H_2^0) may be preferred as more convenient terms when balancing chemical equations (86).

Earlier investigations have shown that most chemical reactions occurring in irradiated aqueous solutions can be explained, at least superficially, by mechanisms involving •H and •OH. In neutral and alkaline solutions more detailed studies on reactions have indicated that \bar{e}_{aq} is to be viewed as the major reducing species (16, 39, 98). Hart (39) proposed that \bar{e}_{aq} is produced by the primary ionization of irradiated water, as:

 $2H_2O \xrightarrow{\gamma} H_3O^+ + \bar{e}_{aq} + \cdot OH$ [2-21]

This combines [2-8] and [2-11]. The \bar{e}_{aq} may be converted to $\cdot H$ under appropriate conditions [2-13].

Conversion of \overline{e}_{aq} to $\cdot H$ is completed even in dilute acids:

$$\bar{e}_{aq} + H^+ \longrightarrow H$$
 [2-22]

In many reactions both \bar{e}_{aq} and $\cdot H$ lead to the same

final products. With a few exceptions, however, e_{aq} is a much more reactive species than $\cdot H$, as can be seen from rate constants in Table 1 (33).

Allen and Schwarz (11) represented the relationship between reducing species, i.e., \bar{e}_{aq} , $\cdot H$ and an acidic form of the hydrogen atom, H_2^+ , as:

$$e_{aq} \xrightarrow{-OH^-} H \xrightarrow{+H^+} H_2^+ \dots \dots \dots [2-23]$$

Work on the radiolysis of monochloroacetic acid by Hayon and Weiss (44) supported the concept of a second reducing species, \bar{e}_{aq} . Hydrogen is a major product from radiolysis of monochloroacetic acid solutions but is replaced by chloride ions in neutral solutions. This can be explained if the reducing species present are \cdot H and \bar{e}_{aq} , as:

 \cdot H + ClCH₂COOH \longrightarrow H₂ + ClCHCOOH [2-24]

$$\bar{e}_{ag}$$
 + ClCH₂COOH \longrightarrow Cl⁻ + ·CH₂COOH .. [2-25]

Regarding differences in chemical behaviour of \bar{e}_{aq} and $\cdot H$, it was observed that \bar{e}_{aq} does not abstract hydrogen atoms from organic compounds, whereas $\cdot H$ does (86).

A prominent role is played by concentration of solutes in aqueous solutions on \overline{e}_{aq} decay kinetics. Decay of \overline{e}_{aq} at low and high concentrations was found to follow second order kinetics, which has been interpreted as indicative of one decay mode (39). Second order kinetics result when:

$$\bar{e}_{aq} + \bar{e}_{aq} \xrightarrow{2H_2O} H_2 + 2OH \dots [2-26]$$

or;

$$\bar{e}_{aq} + \cdot H \longrightarrow H_2 + OH \dots \dots \dots [2-27]$$

In alkaline solution and in solutions containing \cdot OH scavengers, the reaction of \bar{e}_{aq} with \cdot H is inferred from decay curves. On scavenging \cdot OH, the remaining reactant for \bar{e}_{aq} is \cdot H and \bar{e}_{aq} decays by [2-26] and [2-27].

Almost all \overline{e}_{aq} reactions seem to be electron-transfer reactions. In all these cases the primary product acquires an additional electron:

where; A is an atom or a polyatomic molecule and n is an integer indicating charge. Often the primary product is thermodynamically unstable and undergoes futher reactions such as protonation, dissociation, disproportionation or charge transfer. Positive inorganic ions are much more reactive with \bar{e}_{aq} than are negative ones, and the higher the charge the higher the rate constant (33).

2.2.3. Hydroxyl radical (•OH)

Both stationary state and pulse radiolysis investiga-

tions indicate that \cdot OH, which is an oxidizing species, is an important fragment in irradiated water. The \cdot OH arises mainly from rapid reaction of H_2O^+ , which is formed directly during the energy absorption process [2-8].

Dissociation of excited water molecules produced by either direct electron excitation or as a result of electron recapture by the parent H_2O^+ can also form $\cdot OH$ [2-10 and 2-11].

The \cdot OH oxidizing species is produced by photolysis of hydrogen peroxide (H₂O₂), as :

 $H_2O_2 + h_v \longrightarrow 2.0H \dots [2-29]$

Other reactions also lead to production of \cdot OH radicals in radiation chemistry. Thus, the primary reducing species (\cdot H or \bar{e}_{aq}) reacted with H_2O_2 produces \cdot OH radicals (33), according to:

> $H_2O_2 + \cdot H \longrightarrow H_2O + \cdot OH \dots [2-30]$ $H_2O_2 + \bar{e}_{aq} \longrightarrow OH^- + \cdot OH \dots [2-31]$

The conversion of \overline{e}_{aq} to $\cdot OH$ is achieved efficiently by nitrous oxide, as:

$$N_2^0 + \overline{e}_{aq} \longrightarrow N_2 + 0 \dots [2-32]$$

 $N_2 + 0 + H_2^0 \longrightarrow N_2 + 0H + 0H \dots [2-33]$

Four main types of reactions occur between •OH radicals and stable species or free radicals:

- (i) electron transfer;
- (ii) addition;
- (iii) hydrogen atom transfer; and possibly
 - (iv) group abstraction.

Electron transfer is the principal mechanism of \cdot OH-induced oxidation for both inorganic anions and cations. With organic molecules, hydrogen atom abstraction and \cdot OH addition are the most common types of reaction. Addition reactions occur with free radicals (33).

Electron transfer and addition have been observed as examples of anionic oxidation in pulsed radiolysis. For example, the ferrocyanide ion is oxidized to ferric cyanide by •OH, and the latter ion has a strong optical absorption spectrum (3, 30, 40):

 $\operatorname{Fe}(\operatorname{CN})_{6}^{-4} + \cdot \operatorname{OH} \longrightarrow \operatorname{Fe}(\operatorname{CN})_{6}^{-3} + \operatorname{OH}^{-} \dots [2-34]$

Dainton and Watt (30) and Rabani and Matheson (80) indicated that the OH⁻ anion, O⁻, produced at high alkalinity, reacted more slowly with the ferrocyanide ion. They measured the ionization constant of \cdot OH by studying effects of pH on these kinetics.

Adams <u>et al</u>. (4) proposed the formation of 0 via the following reaction:
$\cdot \text{OH} + \text{OH}^{-} \longrightarrow \text{O}^{-} + \text{H}_2\text{O} \dots \dots \dots \dots [2-35]$

The rate constant for [2-35] was found to be 3.6 x 10^8 M^{-1} sec⁻¹. Competitive reactions among OH⁻ and other \cdot OH scavengers determined the amount of O⁻ in solution. The following reaction was found to be very efficient in alkaline solutions:

Adams <u>et al</u>. (2) have observed also a number of transient absorption sepctra resulting from electron transfer from oxyanions of Group IV, V and VI elements. The spectra are due to electron oxidation products in which the elements are in an oxidation state one higher than the reacting solute, as:

$$A_x O_y^{-n} + \cdot OH \longrightarrow A_x O_y^{-(n-1)} + OH^{-} \dots [2-37]$$

Other reactions include those of transient species, such as $S_2O_3^{--}$ from thiosulphate; CO_3^{--} and SiO_3^{--} from carbonate and silicate; NO_2 from nitrite; SeO_3^{--} from selenite; and TeO_3^{--} from tellurite.

The halide ions Cl^- , Br^- and I^- react rapidly with $\cdot OH$. Electron transfer here leads to formation of free radicals:

 $Br + \cdot OH \longrightarrow Br + OH (2-38)$

 $\cdot Br + Br \longrightarrow Br_2$ [2-39]

Numerous cationic electron-transfer reactions are wellknown by which •OH produces stable ions. Thereby, transient spectra for unstable higher oxidation states of many metals have been characterized (33), such as:

 $Fe^{2+} + \cdot OH \longrightarrow Fe^{3+} + OH \longrightarrow [2-40]$

2.2.4. Effects of oxygen

Radiolysis of aqueous solutions is much affected by dissolved oxygen for two reasons.

Firstly, free radicals produced from the solute may react with oxygen, leading to formation of peroxy radicals. The reaction of oxygen with free radical intermediates may change the final products from those obtained in the absence of oxygen. In the case of either organic solutes or organic impurities in aerated aqueous inorganic systems this is usually more important. For example:

where;

R' represents alkyl or allyl groups or hydrogen.

Thus, each \cdot OH brings about the oxidation of 3 Fe⁺³ ions instead of only one. Yield of Fe⁺³ is commensurately higher.

Secondly, oxygen is a very efficient scavenger for hydrogen atoms and combines with them to give the perhydroxyl radical, $\cdot HO_2$. In irradiated aqueous solutions this reaction occurs almost invariably if dissolved oxygen is not completely removed [2-42]. Because of the high probability of this conversion, traces of oxygen modify the course of many radiationinduced reactions. For example, when oxygen is present in the Fricke dosimetric solution [2-42] takes place, as do (86):

$$Fe^{2+} + \cdot OH \longrightarrow Fe^{3+} + OH^{-} \dots [2-40]$$

$$H_{2}O_{2} + Fe^{2+} \longrightarrow Fe^{3+} + \cdot OH + OH^{-} \dots [2-46]$$

$$\cdot HO_{2} + Fe^{2+} \longrightarrow Fe^{3+} + HO_{2}^{-} \dots [2-47]$$

$$HO_{2}^{-} + H^{+} \longrightarrow H_{2}O_{2} \dots [2-48]$$

Therefore, the radiation yield of $G_{(Fe}^{3+})$ is:

$$G_{(Fe^{3+})} = {}^{2G}_{(H_2O_2)} + {}^{3G}_{(\cdot H)} + G_{(\cdot OH)} = 15.6 \dots [2-49]$$

However, in the absence of oxygen, [2-42] is replaced by [2-23] and:

$$\cdot H + H^+ \longrightarrow H_2^+ \dots \dots \dots [2-23]$$

$$H_2^+ + Fe^{2+} \longrightarrow Fe^{3+} + H_2 \dots \dots \dots [2-50]$$

Reactions [2-47 and 2-48] do not occur. For this reason, $G_{(Fe}^{3+})$ in the absence of oxygen is given by:

$$G_{(Fe^{+3})} = 2G_{(H_2O_2)} + G_{(\cdot H)} + G_{(\cdot OH)} = 8.2 \dots [2-51]$$

The \cdot H or \bar{e}_{aq} is replaced by \cdot HO₂ or O₂, i.e., oxygen is a very efficient scavenger [2-42 and 2-52]:

In both above cases, O_2^- can convert reactive species of marked reducing character into less reactive species of mainly oxidizing character. The rate constant for conversion of \cdot H or \bar{e}_{aq} to \cdot HO₂ or O_2^- by O_2 is 2 x 10^{10} M⁻¹sec⁻¹ (33). Form of \cdot HO₂ changes with pH. Neutral, \cdot HO₂, and basic, O_2^- , forms are generally accepted, and pKa values of 4.5 and 4.8 have been reported (33) for the equilibrium:

$$HO_2 \xleftarrow{HO_2} H^+ + O_2^- \dots [2-53]$$

Hence, at high pH values 0_2^- is generally the predominant species.

Oxidation state of $\cdot HO_2$ lies between that for O_2 and H_2O_2 . The $\cdot HO_2$ may behave as either a reducing or oxidizing

agent (33):

 $\cdot HO_2 + Ce^{4+} \longrightarrow H^+ + O_2 + Ce^{3+} \dots [2-54]$

In comparison with \cdot H, \cdot HO₂ is a consistently weaker reducing agent for abstracting hydrogen atoms from saturated organic compounds. Consequently, hydrogen abstraction by \cdot HO₂ is possible only for those hydrogens easily removed, such as with ascorbic acid:

$$\begin{array}{c} HO_2 + R_1 - \begin{matrix} R_2 \\ I \\ C \\ I \\ R_3 \end{matrix} \xrightarrow{H_2O_2} + R_1 - \begin{matrix} R_2 \\ I \\ C \\ R_1 \end{matrix} \xrightarrow{R_2} \begin{matrix} R_2 \\ I \\ R_3 \end{matrix} \xrightarrow{R_2} \begin{matrix} R_2 \\ R_3 \end{matrix} \xrightarrow{R_2} \end{matrix} \xrightarrow{R_2} \begin{matrix} R_2 \\ R_3 \end{matrix} \xrightarrow{R_2} \begin{matrix} R_2 \\ R_3 \end{matrix} \xrightarrow{R_2} \end{matrix} \xrightarrow{R_2} \begin{matrix} R_2 \\ R_3 \end{matrix} \xrightarrow{R_2} \begin{matrix} R_2 \\ R_3 \end{matrix} \xrightarrow{R_2} \end{matrix} \xrightarrow{R_2} \end{matrix} \xrightarrow{R_2} \begin{matrix} R_2 \\ R_3 \end{matrix} \xrightarrow{R_2} \end{matrix} \xrightarrow{R_2} \begin{matrix} R_2 \\ R_3 \end{matrix} \xrightarrow{R_2} \end{matrix} \xrightarrow{R_2} \end{matrix} \xrightarrow{R_2} \begin{matrix} R_2 \\ R_3 \end{matrix} \xrightarrow{R_2} \end{matrix} \xrightarrow{R_2} \begin{matrix} R$$

As an oxidizing agent $\cdot HO_2$ reacts with an $\cdot OH$ radical or another $\cdot HO_2$ radical to produce O_2 (33, 86):

 $\cdot \text{HO}_2 + \cdot \text{OH} \longrightarrow \text{O}_2 + \text{H}_2\text{O} \dots [2-56]$

 $\cdot \text{HO}_2 + \cdot \text{HO}_2 \longrightarrow \text{O}_2 + \text{H}_2\text{O}_2 \dots \dots [2-57]$

2.2.5. Effects of pH

Radiochemical reactions in irradiated aqueous solutions may be greatly influenced by pH. In some solutions pH determines structure of the solute, but in all solutions changes in pH may alter nature and reactivity of primary radicals, formed during radiolysis. The position of equilibrium for substances which are fractionally dissociated in water may shift due to a change in pH. On the other hand, reactive species produced in irradiated water may react much more readily with either the ionized or non-ionized form of the solute.

A prominent role is played by pH on properties of reactive species present in irradiated water. The following pH dependent equilibria have been established for reducing species (86):

- (i) in acid solution the relatively slow association of \cdot H or hydrogen ion (H⁺) [2-23]; and
- (ii) in alkaline solution conversion of $\cdot H$ to e_{aq} [2-23].

For oxidizing species (86):

- (iii) in acid medium [2-11] holds
- (iv) in neutral or mildly alkaline solutions dissociation of $\cdot HO_2$ follows [2-53]

 $HO_2 \xrightarrow{} H^+ + O_2^-$ [2-53]; and

(v) in alkaline solution dissociation of \cdot OH occurs according to [2-35] with pK_a about 10.

Many earlier studies have indicated that pH has considerable effect on yield of reducing species and \cdot OH. The increased radiation yield of radicals, G_R , without corresponding decrease in radiation yield of molecules (molecular hydrogen and hydrogen peroxide), G_M , at pH below about 3 has been accepted without argument (Fig. 1, 2 (19)). At high pH (above about 11), however, increase in G_R was observed with slight decrease in the yield of H_2O_2 in previous studies. Recently Draganić and Draganić (33) proposed that G_R and G_M values in irradiated aqueous systems do not change above pH 13. For above pH 13:

$$G_{-H_2O} = 4.09$$
 $G_{H+\bar{e}_{aq}} = 3.18$
 $G_{\cdot OH} = 2.72$ $G_{H_2} = 0.45$
 $G_{H_2O_2} = 0.68$

The increase in acidity induces an increase in water decomposition. For example, at pH 1.3 the following values were derived:

> $G_{-H_2O} = 4.35$ $G_{H+\overline{e}_{aq}} = 3.49$ $G_{\cdot OH} = 2.85$ $G_{H_2} = 0.43$ $G_{H_2O_2} = 0.76$

In general, primary yields do not depend much upon pH (Fig. 2), but do relate to solute concentration. The increase in G_R below pH 3 may be attributed to the relative abundance of \cdot H compared to \bar{e}_{aq} . This may affect G_R values at extreme pH readings, since species produced by conversion have different coefficients and different recombination rate constants in acid media for $G_{\bar{e}_{aq}}$ [2-13]. Hence, fewer \bar{e}_{aq} are combined with \cdot OH to form non-radical products by the following reaction (98):

 $e_{aq} + \cdot OH \longrightarrow H_2O + OH^-$ [2-58]

Dainton and Peterson (29) have interpreted increased G_R in acid solutions as due to attack upon the acid by an intermediate. The intermediate is either an excited water molecule, H_2O^* , or an isolated radical pair, $\cdot H$ and $\cdot OH$, trapped in a solvent cage, as:

 $H_2O^* + \cdot H \longrightarrow H_2^+ + \cdot OH \dots [2-59]$

or;

 $(\cdot H + \cdot OH) + H^+ \longrightarrow H_2^+ + \cdot OH \dots [2-60]$

The above reactions reduce the extent of [2-16] and the following reverse reaction:

Czapski (27) concluded that in many cases where G-value

seemed to depend on pH or on scavenger concentration, effects actually resulted from disregarded back reactions. There is no strong dependence of primary yield on pH, although the situation at extreme pH is not yet clear. In this connection it should be noted that effects at extremely high acidity or alkalinity represent special problems which require particular study.

2.2.6. Scavengers

If a substance Q reacts preferentially with the primary radical $\cdot R$, formed in irradiated water, to give the product P according to the reaction:

then increase of [Q] should be followed by increase in stable final product yield $G_{(P)}$. This increasing process should continue until all $\cdot R$ species escaping recombination:

 $\cdot R + \cdot R \longrightarrow M$ [2-63]

are scavenged.

Scavenging is the term applied to the deliberate addition to a radical reaction of a compound which reacts preferentially with radicals, at the expense of the normal radical reaction. The objective is to identify the radical species taking part in the reaction and to determine what part of the overall reaction is due to scavengeable free radicals. Using moderate scavenger concentrations, the scavenging action will be limited to radicals which have diffused into the bulk of the sample. Reactions in the track zone will be unaffected, thereby allowing the reactions in these two regions to be differentiated (86).

Effectiveness with which the scavenger reacts with the species $\cdot R$ above also depends on reaction rate constant $K_{R+\varphi}$ (reactivity is usually represented as $K_{R+\varphi} \cdot [\phi] \cdot \sec^{-1}$). Consequently, scavenger concentration, ϕ , in the irradiated solution is very important if $G_{(P)}$ is to be taken as a measure of G_{R} .

Scavengers do not react with all radicals at very low concentrations $(10^{-5} \text{ to } 10^{-4} \text{ M})$. Other reactions between them and molecular products or impurities may also play an important role, not always easily controlled.

At moderately low concentrations, scavengers remove all those radicals which are in the bulk of the solution. When reactivity is sufficiently high, scavenger Q also competes for •R species from intra-spur reactions. Then an increase in G_p begins to occur because of G_M . The increase in concentration of a substance reacting with •OH leads to decreased yield of H_2O_2 . When the substance is reacted with •H or \bar{e}_{aq} the yield of H, is decreased (33).

In concentrated solutions the direct action of radiation on solute might introduce uncertainties as to the reaction

scheme. This direct effect might also occur by the interference of solutes in earlier stages of radiolysis rather than allowing intra-spur reactions. For the present, such effects are not well established (33).

Dependence of radical yields on solute concentration for a number of solutes including NO_3^- , I⁻ and Ti⁺, as well as N_2^{O} , has been studied by Hayon (43). In every case the data show that $G_{\cdot H+\bar{e}_{aq}}$ and $G_{\cdot OH}$ increase with increasing concentration of solute (43).

Nitrous oxide (N_2^{0}) is widely used as an electron scavenger because of efficiency of reaction [2-32] and because the inert product nitrogen (N_2) affords a convenient measure of G.

In early investigations on radiolysis of N₂O solutions, Dainton and Peterson (29) found that as N₂O concentration was increased $G_{(N_2)}$ increased to a plateau value of 3.1 for N₂O concentrations larger than 1.3 x 10⁻²M. Recently, Head and Walker (45) studied $G_{(N_2)}$ as a function of N₂O over the range $O<[N_2O]<1.2 \times 10^{-2}$ M. They observed that for low concentrations $G_{(N_2)}$ increased rapidly from 0 to 2.45 as N₂O concentration was raised to 4 x 10⁻⁵ M. The reaction then followed a slower $G_{(N_2)}$ increase from 2.45 to 3.1 as N₂O concentration was raised to 1.2 x 10⁻² M. These results were interpreted as indicating that efficient scavenging at low N₂O concentration represents reaction [2-32]. Hence, $G_{(N_2)} = G_{(\bar{e}_{aq})} = 2.45$. The second and slower rise was attributed to scavenging of a second radia-

tion product entity, rather than intra-spur scavenging of \bar{e}_{aq} . This second species was not identified by the authors. It seems unlikely that it could be \cdot H, since Mahlman (60) has reported that for saturated N₂O solutions G_(N2) is unaffected by the presence of efficient \cdot H scavengers such as 2-propanol and sodium formate. On the other hand, it has been suggested (19, 28) that the following may be a source of N₂ at high N₂O concentration:

 $H_2O^* + N_2O \longrightarrow N_2 + 2OH \dots [2-64]$

In N₂O saturated solutions at room temperature, its concentration is about 2.5 x 10^{-2} M. Clearly, under these conditions $G(N_2) = G(\bar{e}_{ag})$.

2.2.7. Other effects

It is evident that chemical effects of ionizing radiation depend upon rate at which ionization occurs in the aqueous medium. The density of spurs will depend upon intensity of ionizing radiation. Chemical effects will depend in turn upon this intensity or dose rate. In other words, increased dose rate should have effects on radiation yield similar to those observed in the case of LET, since increased density of primary events is involved. Therefore, yields of stable reaction products should increase or decrease, depending upon whether these are formed by reactions with molecular or radical products (33). Increase of temperature might lead to a broader distribution of primary species and, thereby, to increased G_R and decreased G_M . According to Hochanadel and Ghormley (48), changes caused by increased temperature are indeed in agreement with these expectations. Since changes are small, however, it is understandable why usual variations of room temperature have no appreciable effect on measured yields of primary products. Similarly, the effect of temperature on reaction rate constants is small. These increase by only a few tenths of a per cent per degree.

Increased pressure causes considerable structural change in water. However, Hentz <u>et al</u>. (46) concluded that there is no pressure effect on the primary yields of free radicals and molecular products in acid medium. The rate constants of some of the reactions studied were found to be appreciably affected by changes in pressure, although no effect of pressure on the primary yields from water radiolysis could be proven.

2.3. Radiolysis of Inorganic Sulphur Compounds in Aqueous Environment

Radiolysis of aqueous solutions for many inorganic compounds have been studied. Systems discussed here are those which are chiefly anionic. Specifically, this short review considers only sulphur containing anions.

Concerning the radiolysis of anions in aqueous media,

the presence of \cdot OH with high oxidizing power or \cdot H (or \overline{e}_{aq}) with high reducing power probably causes most anions to undergo electron transfer reactions, such as:

 $A^{-} + \cdot OH \longrightarrow A + OH^{-} \dots [2-65]$ $A + \bar{e}_{aq} \longrightarrow A^{-} \dots [2-6\bar{6}]$ $(A + \cdot H \longrightarrow A^{-} + H^{+})$

The radiolysis of aqueous inorganic sulphur solutions has been of some recent interest. In constrast to nitric and perchloric acid, sulphuric acid is relatively stable to radiation (31). In dilute or moderately concentrated solutions of sulphuric acid, peroxysulphuric acids are formed, i.e., H_2SO_5 and $H_2S_2O_8$. A product with reducing properties similar to hydrogen was identified, but there was no evidence for presence of SO_2 (31). However, Hochanadel <u>et al</u>. (49) did find evolution of SO_2 upon irradiation of aqueous sulphuric acid solutions of varying concentrations. These investigators found decreased rate of SO_2 production with increased dose. Addition of hydrogen peroxide or oxygen to the solution also diminished SO_2 formation.

Packer (76) irradiated aqueous H_2S solutions with ${}^{60}CO \gamma$ -rays. The products found were S_O , SO_4^{--} , H_2 and H_2O_2 . Complete scavenging of $\cdot H$ and $\cdot OH$ radicals was assumed in the mechanism proposed:

H ₂ S	+	•ОН	>	•HS +	^H 2 ^O	• • • • •	[2-67]
H ₂ S	+	• H	>	•HS +	H ₂	••••	[2-68]
2•HS			>	H ₂ S +	۰s	• • • • •	[2-69]

Both presence of O_2 and increased concentration of H_2S produced a rise in $G_{(S_0)}$. Packer (76) suggested a chain mechanism involving the reactions:

The \cdot HSO₂ probably react rapidly among themselves and with H₂S and H₂O₂ to yield \cdot S and SO₄⁻⁻.

Aqueous potassium thiocyanate solutions have been irradiated with γ -rays from 60_{CO} sources (34). The products were CN⁻, SO₄⁻⁻ and S_O. Since yield of sulphur did not increase with concentration of potassium thiocyanate, formation of S_O was attributed to indirect action.

Abellan (1) studied the effect of $60_{CO} \gamma$ -radiation on Na₂S₂O₃ alkaline solutions. The radiolysis products reported were SO₃⁻⁻ and H₂S gas. Presence of S₀ was noted only at higher doses. The acid was estimated potentiometrically by decrease in solution alkalinity. As a measure of SO₃⁻⁻ and H₂S gas quantities formed, iodometric estimation of the increase

in reducing power was taken. Removal of H_2S gas by bubbling N_2 permitted estimation of SO_3^{--} ions alone. The following mechanism was suggested:

 $2S_2O_3^{--} + 4 \cdot OH + 2 \cdot H \longrightarrow HS^{-} + 3SO_3^{--} + 3H^{+} + H_2O \dots [2-72]$

Here, $G_{(S_2O_3^{--})}$ was found to increase with concentration and its asymptotic limit was reached at 0.06 M.

It has been shown by Ivanitskaya and Nanobashvili (50), Murthy (65) and Natroshvili and Nanobashvili (70) that in radiation of $Na_2S_2O_3$ solutions SO_4^{--} , SO_3^{--} and S_0 are formed with G-values of 0.8 ± 0.1, 0.55 ± 0.1 and 0.16 ± 0.02, respectively, while $G_{(-Na_2S_2O_3)}$ is 0.65 ± 0.12. The intermediate formed is SO_3^{--} and end products are SO_4^{--} and S_0 . If irradiation is done in the presence of N_2O , $G_{(-Na_2S_2O_3)} = 2.95$. A radical mechanism is involved with $\cdot OH$ formed as a reactive intermediate in the irradiated water during radiolysis of aqueous $Na_2S_2O_3$ solutions.

Nanobashvili <u>et al</u>. (68, 69) investigated radiolytic oxidation and reduction of sulphur compounds. Main chemical effects of high energy radiation on dilute aqueous solutions were formation of \cdot H and \cdot OH. The oxidative effects of x- and γ -irradiation on various classes of sulphur compounds, aqueous solutions of sulphides and thiocyanates of alkali metals have been studied. The HS⁻, S⁻⁻, [Fe(CN)₆]⁻³, [Fe(CN)₆]⁻⁴ and CNS⁻ ions become oxidized by \cdot OH or H₂O₂ molecules. The G-value was dependent on concentration and radiation intensity, which indicates that a chain reaction mechanism has taken place.

No reference to polysulphide formation in aqueous sulphide solutions by radiation has been found in the literature. However, several investigations on γ -radiolysis of sulphur containing organic compounds have shown disulphides to be formed as main conversion products (22, 72). Nishimura et al. (72) have investigated γ -radiolysis of characteristic sulphoxide amino acids in Allium species, e.g., PCSO (s-n-propyl-L-cystein sulphoxide). Di-n-propyl disulphide, alanine and cysteic acid formed as main products from PCSO irradiated in oxygen-free aqueous solutions were identified by IR and mass spectrometry. In order to elucidate degradation mechanism for the deoxygenated volatile products (di-n-propyl sulphide and di-n-propyl disulphide) obtained from irradiated PCSO, 20 M oxygen-free aqueous solutions of various PCSO concentrations containing N2O (specific scavenger for \bar{e}_{ag}) or KBr (specific scavenger for •OH) were irradiated. As a result it was proposed that PCSO reacts with •OH and with both \bar{e}_{ac} and •OH to produce di-n-propyl sulphide and di-n-propyl disulphide, respectively.

3.0. MATERIALS AND METHODS

A series of irradiation experiments was carried out with aqueous sodium sulphide (Na₂S) solutions and additives; such as nitrous oxide (N₂O), 2-propanol (CH₃CHOHCH₃), oxygen (O₂) and hydrogen sulphide (H₂S). Nitrogen gas (N₂) was bubbled through the system to remove oxygen.

Following irradiation treatments, polysulphide analyses were done by the UV spectrophotometric technique and $G(S_nS^{-})$ values were calculated.

3.1. Sample Preparation

All chemicals were of the best grades available; N_2O , N_2 and O_2 of medical therapy grade were obtained from Matheson of Canada; analytical grade Na_2S and $CH_3CHOHCH_3$ were purchased from Fisher Chemical Co. Solution pH was adjusted, where desired, with reagent grade H_2SO_4 . Purified distilled water was obtained from the Chemistry Department, Univ. of B.C. This ultra-high purity water was further treated by irradiation with 1 Mrad to destroy any trace organic impurities.

The Na₂S·9H₂O contained 1 to 2% impurities as oxidation products, among which Na₂S₂O₃, Na₂SO₃, Na₂S₂ and NaOH are the most common. To obtain pure anhydrous Na₂S, the Na₂S·9H₂O was first heated slowly under vacuum to 300° C to remove hydration water, then further heated to 600° C to remove the remaining water and impurities (83). The anhydrous product thus obtained was white and repeat analyses according to Bethe

(17) indicated a value of 100.0 ± 0.2 % Na₂S. The white color was also an indication of high purity. For instance, the presence of as little as 0.1% polysulphide was found to cause noticeable discoloration.

Aqueous solutions were made with the treated ultrahigh purity water and prepared anhydrous Na_2S . To prevent reaction with other impurities, and to obtain a high cationic concentration for polysulphide stabilization, 10^{-3} M NaCl was added to these solutions. Working concentrations of Na_2S solutions were 10, 40 and 80 g/l. Initial pH of the corresponding solutions was 12.7. Solutions at pH 1.0 and 7.0 were made by adding H_2SO_4 . All pH measurements were made on a Radiometer Type M 26 pH meter.

Samples (50 ml) of the above solutions were introduced into Erlenmeyer flasks which were sealed in a stainless steel (SS) vessel. Gas (N_2 , N_2O , H_2S , O_2) was admitted to the vessel as required.

Sample solutions examined in this study can be classified according to the following four groups:

- (i) Na₂S solutions (40 g/l at initial pH12.7) without additives;
- (ii) Na₂S solutions (10, 40 or 80 g/l at initial pH 12.7, 40 g/l at initial pH 1.0 and 7.0) with •OH and ē aq scavengers;
- (iii) Na_2S solutions with scavengers and H_2S at initial pH 12.7; and

(iv) Na₂S solutions with H_2S at initial pH 12.7.

Certain preparatory experiments were done to test suitability of the systems used. A SS high pressure cell of internal diameter 50 mm and 100 mm depth, and containing a truncated Erlenmeyer flask as container, was used (Fig. 3). The gasification apparatus is shown in Fig. 4.

Prior to each experimental series the whole glass apparatus was cleaned. First, it was cleaned by soaking in permanganate-acid (KMnO₄ in 95% H_2SO_4) and then rinsed with distilled water. Second, it was soaked in a biodegradable detergent solution to remove acidic traces, rinsed in tap water, then distilled water and, finally, with the treated ultrahigh purity water. Following this, the apparatus was dried in an oven at 150°C and stored in dust free atmosphere.

3.2. Sample Irradiation

Cobalt-60 γ -rays from a Gamma Cell 220 were used to irradiate the solutions, which were at 34° C and kept under a gas pressure of 20 psi during irradiation.

Solutions were first deoxygenated by bubbling N_2 through the system for about 20 min before purging for 20 min with experimental gas to completely remove N_2 . The solution was then pressurized to 20 psi. At this pressure virtually all gas dissolved in the solution. The pressurized sample was left to equilibrate for about 1 hr. During irradiation, a glass-diffusion tube was used in order to provide mixing of the liquid and pressurized gas in the flask. Irradiation dosages ranged from 0.02 to 20 Mrad.

After irradiation, the vessel was slowly depressurized through the trap system, the SS vessel cap was removed and the solution was analyzed.

In order to determine the absorbed dose, several methods may be employed. For these experiments, Fricke dosimetry was used.

Dose rates of the Cobalt-60 source inside and outside the SS vessel were determined by Fricke chemical dosimetry as first proposed by Fricke in 1929 and since modified by others (86).

Fricke dosimetry utilizes an air saturated solution of ferrous sulphate in 0.8 N H_2SO_4 to measure absorbed dose. In the acidic solution the two primary reducing species, \bar{e}_{aq} and H atoms, are converted to oxidizing species by [2-13, 2-42 and 2-43] or the following reactions:

 $H^{+} + H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + \cdot OH + H_2O \dots [3-1]$

 $H^+ + \cdot OH + Fe^{2+} \longrightarrow Fe^{3+} + H_2O \dots [3-2]$

Thus, each \cdot H formed from [2-13] leads to oxidation of 3 Fe²⁺, whereas each \cdot OH oxidizes only 1 Fe²⁺. For Cobalt-60 γ -rays the total G-value of Fe³⁺ has been determined as

 $G_{(Fe}^{3+}) = 15.5$ (86). The ferric ion is determined spectrophotometrically at 304 nm, where the molar extinction coefficient (ϵ) is 2,197 M⁻¹cm⁻¹ at 25°C. ϵ increases by 0.69% for each degree increase in temperature.

Absorbed dose, D (in rad), is calculated by the following general formula (33):

$$D = \frac{N \Delta (OD) 100}{\varepsilon \cdot 10^3 \cdot G_{(Fe^{3+})} \cdot f \cdot p \cdot 1} \text{ rad } \dots [3-3]$$

where:

f

- N = Avogadro's number at 6.022 x 10²³ molecules per mole;
- Δ(OD) = difference between optical densities of irradiated and control samples;

- = conversion factor for transition from
 electron volts per mililitre units
 into rad (6.245 x 10¹³);

1 = optical path length in cm.

The ferrous sulphate dosimeter is very sensitive to traces of organic impurities. When organic material (\mathring{R} H) is present [2-41 to 2-45] may occur. Thus, each \cdot OH brings about the oxidation of 3 Fe³⁺ instead of only one, and the yield of Fe³⁺ is commensurately higher, i.e., $G_{(Fe^{3+})} > 15.5$. This leads to errors in determination of dose or dose rate. To suppress [2-41] Cl⁻ is normally added to the dosimeter solution:

 $\cdot \text{Cl} + \text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + \text{Cl}^{-} \dots [3-5]$

Since Cl⁻ is in high concentration relative to organic impurities the fate of \cdot OH will be reaction [3-4], rather than [2-41]. Because of the effect of \cdot Cl on Fe²⁺, i.e., equivalent effect to \cdot OH, there will be no change in G_{(Fe}3+) (86).

If oxygen is not present in the solution, [2-42] and [2-43] will not occur. The result is that $G_{(Fe^{3+})}$ becomes 8.2 (86).

Dosimetry results for irradiation in the high pressure SS cell are plotted as the absorbance \underline{vs} . irradiation time in Fig. 5. From slope of the line, and taking $G_{(Fe^{3+})} =$ 15.5, dose rate inside/outisde the SS vessel was calculated by [3-3] to be 8.876 x 10^3 / 12.24 x 10^3 rad per minute on March 10, 1972. Subsequent corrections were made for variation in dose rate due to source decay.

3.3. Analyses

Standard polysulphide solutions were prepared by heating known amounts of purified anhydrous Na₂S together with l g/l of sublimated sulphur in ethanol. Polysulphide in ethanol is known to have an X_s value of about 7 (88). After the ethanol was evaporated under vacuum at 50°C, an appropriate amount of boiled distilled water was added. To avoid oxidation of S_nS^- to $S_2O_3^{--}$, the solution was left standing with the suspended sulphur overnight under nitrogen. Subsequent removal of the suspended sulphur together with the impurities by filtration is known (88) to result in a polysulphide solution having a high X_s value (\approx 4), low $S_2O_3^{--}$ content (<0.005 moles /1) and low alkalinity (0.001 M OH⁻/1). The solution thus obtained was stored under a layer of paraffin oil.

The characteristic absorbance of S_s⁻ at 285 nm wave length was measured with a Unicam SP 800 UV Spectrophotometer using trough-like silica cells of 0.01, 0.2 and 1.0 cm path Most of the solutions could be studied without lengths. dilution throughout concentration ranges encountered in this work by using these cells of varying path length. Due to the strong absorptivity of polysulphide, and instability of very dilute polysulphide solutions, the usual 1.0 cm cells are unsuited for measurements at high polysulphide concentrations (15, 37, 89, 91, 94). Since polysulphide concentration is known to be dependent on the sodium sulphide concentration (15), three calibration curves were prepared corresponding to Na₂S concentrations (10, 40 and 80 g/l) used in the study. Peak heights in relative units at 285 nm absorbance were plotted against polysulphide excess sulphur concentration to give calibration curves (Fig. 6). These plots of absorbance <u>vs</u>. polysulphide excess sulphur followed Beer's law.

Spectrophotometric polysulphide analyses were performed on the various experimental solutions according to the method of Teder (89). Some solutions were diluted with corresponding original stock solution before measurements could be done. An alkaline 3 M NaCl $(10^{-2}$ to 10^{-3} M OH⁻ + 3 M NaCl) solution was used as reference.

For wave length calibrations in the ultraviolet region an absorption spectrum was obtained by measuring absorbance of a 2 mm thick piece of holmium oxide glass (14).

Since with even the greatest of care, small amounts of polysulphide were formed in stock solutions, experimental data were adjusted accordingly.

Cleaning of UV cells between measurements was as follows. First, all traces of sample solution were removed and the cells were washed in carbon disulphide (CS₂) and distilled water. Second, a washing was done with concentrated nitric acid (HNO₃) in an ultrasonic bath, followed by rinsing with distilled water. Several changes of hot and cold distilled water were used. Third, the cells were rinsed thoroughly in cool reagent grade ethanol, and allowed to dry while protected from dust contamination.

From 3 to 5 replications were done for each treatment. Although substantial yields of polysulphide were observed to accompany treatments, the results were not entirely reproducible. In addition, it was not possible to determine exactly how much polysulphide was produced in the solution alone, since at all times this was under an over-gas.

The concentration of polysulphide excess sulphur in the sample was calculated from absorbance as follows (89):

 $C = \frac{A}{Eb} \qquad [3-6]$

where:

C = concentration of polysulphide excess sulphur in the sample, g-atom litre⁻¹;

A = absorbance;

- $E = absorptivity = 1,360 \text{ litre, cm}^{-1}$ (g-atom excess sulphur)⁻¹; and
- b = path length of the cell (cm).

In order to express the yield of a species or product formed by radiolysis the term "G-value" is used. G-value is defined as the number of molecules, ions, atoms or radicals produced (or consumed) per 100 eV of energy absorbed by the radiation.

In this system, G-value was calculated as the number of sulphur atoms associated per 100 eV radiation energy. Since polysulphide excess sulphur is a heterogeneous compound, its exact molecular weight cannot be easily determined by normal chemical analysis. Thus, the G-value is also an expression of X_{c} value.

For "primary" species or "molecular" products, the

notation " G_X " is generally used and G_X is normally in the range of 0 to 10. For secondary processes involving chain reactions it is not usual for a G-value to exceed 10.

It is necessary to know the total amount of energy absorbed by the system in order to measure the G-value of any species formed by radiation. This amount of energy is termed the "absorbed dose" which is expressed in a variety of units, among which "rad" is commonly used. One rad is defined as the equivalent of 100 ergs per gram in energy.

G-values were obtained from the initial slope on graphs of polysulphide yield vs. radiation dose.

4.0. RESULTS

The role of \cdot OH and \bar{e}_{aq} on formation of polysulphide was studied by using scavengers. Effects of radiation dose, Na₂S concentration, pH, H₂S over-pressure and O₂ on polysulphide yield were also studied (Fig. 7 to 17).

The mechanism of polysulphide formation from aq Na₂S solutions by γ -radiation was investigated by using N₂O as an \bar{e}_{aq} scavenger and 2-propanol as a \cdot OH scavenger (Fig. 7, 9 to 13, 16 and 17). An aq 40 g/l Na₂S solution without scavengers was found to have $G_{(S_nS^{--})}$ value of 0.75 ± 0.01. Adding N₂O gave the much higher $G_{(S_nS^{--})}$ value of 5.79 ± 0.6, while a $G_{(S_nS^{--})}$ value of 0.39 ± 0.01 was obtained for the comparable 2-propanol system (Fig. 8, 11 and 13 and Table 2).

Dependence of radiation yield on absorbed dose for aq Na_2S solutions is given in Table 2. The absorbed dose is expressed in Mrad, while yields are given in g/l. $G_{(S_nS^{--})}$ values were calculated by plotting polysulphide yields as functions of absorbed dose.

It is observed from dose-yield relationships that yield per unit absorbed dose increased directly with dose, except in O_2 addition experiments. The highest yield obtained was 14 g/l polysulphide from 20 Mrad irradiation of the 80 g/l aq $Na_2S - N_2O - H_2S$ system (Table 2).

Solute concentrations of Na₂S solutions used were 10,

40 and 80 g/l. For the 10 g/l aq Na_2S solution, $G_{(S_nS^{--})}$ was founded to be 1.35 ± 0.2. A G-value of 7.84 ± 0.8 was obtained for the 80 g/l solution, and for the 40 g/l solution a larger range of $G_{(S_nS^{--})}$ values were observed depending upon the experimental system used (Fig. 7, 16 and 17, and Table 2).

The effect of pH (1.0, 7.0 and 12.7) on radiation yields was also studied. The G-value at pH 12.7 was 5.79 ± 0.6 for the 40 g/l aq Na₂S - N₂O system. The comparatively lower Gvalues at pH 1.0 were 0.63 \pm 0.01 for Na₂S - N₂O, and 0.53 \pm 0.01 for Na₂S - 2-propanol systems. The highest G-value in the pH series studied was 10.06 \pm 1.0, found with the 7.0 pH 40 g/l aq Na₂S - N₂O (Fig. 9 to 12 and Table 2).

The effect of H_2S on polysulphide yield was also studied. As noted in the case of the 40 g/l aq $Na_2S - N_2O$ system, the G-value obtained was 5.79 ± 0.6; for the 40 g/l aq $Na_2S - N_2O H_2S$ system the G-value was 7.23 ± 0.7. This increase suggests an additive effect of hydrogen sulphide on formation of polysulphide (Fig. 11 and 16 and Table 2). This system also gave the second highest concentration of polysulphide among experiments tried (10.5 g/l at 20 Mrad).

Oxygen saturated aq Na_2S solutions showed an increase in radiation yield with $G_{(S_nS^{--})}$ in this case at 108.30 ± 5.0 over the lower dose range. At higher doses, however, the G-value appeared to decrease (Fig. 15 and Table 2).

The relative errors of the G-values were considered to be ± 5 to 10% of their calculated values.

5.0. DISCUSSION

This thesis compares polysulphide G-values determined from radiation yields obtained under various experimental conditions; and attempts to describe some features of mechanism in polysulphide formation by radiation. First, mechanism is discussed, then factors which affect these reactions are discussed.

5.1. Mechanism of Polysulphide Formation

Radiation yield of polysulphide was not significantly higher for 80 g/l aq Na₂S solutions than for 40 g/l solutions (Fig. 16 and 17 and Table 2). Consequently, the radiolysis of aqueous sodium sulphide solutions used did not give any direct effect of radiation on the nature of polysulphide formation.

Water is the main component of dilute aqueous systems, and one has to consider mechanisms involving products resulting from γ -radiolysis of water. As discussed, these products are excited water molecules (H₂O*) and various reactive intermediates, such as \cdot H, \cdot OH, \bar{e}_{aq} and H₂O₂. Thus a mechanism involving indirect radiation effects may proceed from excited water molecules and from formation of intermediate molecules.

In radiolysis of aqueous solutions the contributions made by excited water molecules to observed chemical changes are generally regarded as negligible (33). The reactions involving excited water molecules may proceed as:

An aqueous sodium sulphide solution consists of the following components:

$$Na_2S + H_2O \longrightarrow Na^+ + SH^- + Na^+ + OH^- ...[5-2]$$

 $SH^- + OH^- \longrightarrow S^- + H_2O[5-3]$

SH

$$SH^{-} + H_2^{O} \xrightarrow{H_2^{S} + OH^{-}} \dots [5-4]$$

The excited water molecules, in turn, may transfer energy to SH (or S) ions.

$$H_2^{O*} + SH^- \longrightarrow H_2^{O} + (SH^-) * \dots [5-5]$$
$$H_2^{O*} + S^{--} \longrightarrow H_2^{O} + (S^{--}) * \dots [5-6]$$

The excited (SH⁻)* or (S⁻)* ions may either revert to the ground state by losing excitation energy to the surroundings or else undergo the following reactions:

> (s⁻⁻) * → s⁻⁻[5-9]

The radicals and ions, which are formed with low energy in the above reactions, recombine and dissipate the energy of recombination as heat without evident chemical change. If the above

were the only reactions, steps involving excited species would not give rise to new products.

Most chemical changes observed in the radiolysis of aqueous solutions can be explained by means of reactive intermediates formed in irradiated water. These intermediates are summarized [2-20]. The molecular products H_2 and H_2O_2 are produced in small amounts. The nature and amount of intermediates formed in irradiated water depend on various factors, such as solution pH, presence of oxygen and the nature of the solute. Thus consideration has to be given to reactive intermediates formed in irradiated water, especially at higher pH, such as 12.7. At this pH level the predominant species are expected to be \bar{e}_{aq} and $\cdot OH$ radicals. However, a few $\cdot H$ from primary events in water radiolysis and a small amount of H_2O_2 will also be present.

In order to examine the roles of the \bar{e}_{aq} and \cdot OH radical in polysulphide formation, N₂O was used as an electron scavenger and 2-propanol was used as an \cdot OH scavenger.

Conversion of \bar{e}_{aq} into \cdot OH is efficiently achieved by nitrous oxide, since N₂O in the system enhances the amount of \cdot OH radicals in the H₂O radiolysis as [2-32, 2-33, 2-64] and:

 $\cdot H + N_2 O \longrightarrow N_2 + \cdot OH \dots [5-10]$

A common radiation - induced reaction of alcohols (R_1R_2-C-OH)

is loss of an α -hydrogen atom to give the radical $R_1 R_2 - C - OH$ (86) such that:

$$\begin{array}{c} \text{OH} & \text{OH} \\ \text{CH}_3 - \dot{\zeta} - \text{CH}_3 & \xrightarrow{\gamma} & \text{CH}_3 - \dot{\zeta} - \text{CH}_3 + \cdot \text{H} & \dots & [5-11] \\ \text{H} \end{array}$$

and the radicals formed react as [2-16] and :

$$\begin{array}{c} \text{OH} & \text{OH} \\ \text{CH}_3 - \overset{\circ}{\xi} - \text{CH}_3 + \cdot \text{H} & \longrightarrow & \text{CH}_3 - \overset{\circ}{\xi} - \text{CH}_3 + \text{H}_2 & \dots & (5-12) \\ \text{H} & \\ & \text{K} = 2 \times 10^7 \times \text{M}^{-1} \text{ sec}^{-1} \end{array}$$

$$CH_{3} \xrightarrow{\text{OH}} CH_{3} \xrightarrow{\text{OH}} CH_{3} \xrightarrow{\text{OH}} CH_{3} \xrightarrow{\text{OH}} CH_{3} \xrightarrow{\text{OH}} H_{2} O \dots (5-13)$$

$$CH_3 - \dot{C} - CH_3 + OH \longrightarrow CH_3 - \dot{C} = CH_2 + H_2O \dots (5-14)$$

Thus, 2-propanol strongly suppresses the \cdot OH radical, whereas N₂O increases \cdot OH yield.

From experimental results (Fig. 8, 11, 13 and Table 2), it is strongly suggested that the 'OH radical initiates the polysulphide reaction. Polysulphide formation was enhanced by adding N_2O and was decreased by adding 2-propanol. Since all experiments were conducted in the absence of air, the oxidizing species can be considered to be $\cdot OH$ radicals and H_2O_2 formed in irradiated water.

The role of oxidizing intermediates in polysulphide formation requires some discussion. In aqueous solution the Na₂S reacts with H_2O (59) according to [5-2] or:

 $Na_2S + H_2O \xrightarrow{} NaOH + NaSH \dots [5-16]$

The anion S^{-} and H_2^0 then react according to [5-3] and [5-4].

Because OH⁻ ions enter into these equilibria, the extent of ionization depends on pH. It is known that at pH=7, H_2S is present mainly as H_2S ; while at pH = 11 to 13, such as in kraft pulping (pH = 12.7 in the present work), H_2S is mainly present as SH⁻ ion from the 1st and 2nd ionization constant (59, 76). Since in the pH range of kraft pulping formation of H_2S is negligible (59, 76), these anions could react with intermediates formed by water radiolysis, to yield polysulphides in the following ways:

 $SH^{-} + \cdot OH \longrightarrow SH + OH^{-} \dots [5-17]$ $\cdot SH + \cdot OH \longrightarrow S + H_2O \dots [5-18]$ $\cdot S + S^{-} \longrightarrow S_2^{--} \dots [5-19]$



It is possible, however, that some •S might be converted to elemental sulphur by the following reaction:

$$\cdot s \longrightarrow \frac{1}{8} s_{08} \dots (5-24)$$

This elemental sulphur, in turn, might produce:

$$s_0 + s^- \longrightarrow s_2^- \dots (5-25)$$

 $ns^0 + s^- \longrightarrow s_n s^- \dots (5-26)$

or;

 $nS^{\circ} + SH^{-} + OH^{-} \longrightarrow S_nS^{--} + H_2^{\circ} \dots [5-27]$

Due to high concentrations of Na_2S , most $\cdot S$ formed would probably recombine with S^- or HS⁻ to yield S_nS^{-} .

$$HS^{-} + \cdot OH \longrightarrow H_2O + S^{-} \dots [5-28]$$

$$S^{-} + \cdot HS \longrightarrow HS_2^{-} \dots [5-29]$$

$$HS_2^{-} + \cdot HS \longrightarrow H_2S_3^{-} \longrightarrow S_n^{--} \dots [5-30]$$

 H_2O_2 itself, as an oxidizing species formed in irradiated water, can produce additional radicals, as well as initiate the reaction for polysulphide formation [2-30, 2-31 and 5-17] and:

• SH	+ 2.0H	$\cdot \text{HSO}_2 + \text{H}_2 \cdots$	[5-31]
• SH	+ H ₂ O ₂ →	$\cdot \text{HSO}_2 + \text{H}_2 \cdots$	[5-32]
•HSO2	+ •SH→	$H_2 SO_2 + \cdot S \dots$	[5-33]
^H 2 ^{SO} 2	+4.OH	$SO_4^{} + 2H_2^{-}O + 2H^+$.	[5-34]
s	+ 2·OH →	so ₂ + H ₂ ···	[5-35]
s	+ ^H ₂ ^O ₂ →	so ₂ + H ₂	[5-36]
۰S	+ so ₂	s ₂ o ₂	[5-37]
s202	+ • OH	HS ₂ 0 ₃	[5-38]
			1

As shown in the scavenger experiments, the role of \bar{e}_{aq} seems to be negligible in polysulphide formation. Its importance is in reducing intermediates through the reaction of S⁻⁻ with reducing species. In some cases the reducing species (·H atoms and \bar{e}_{aq}) react with the same solute to give different products (44).

The present work at pH = 12.7 includes \bar{e}_{aq} as the major reducing species. At this pH the conversion of \bar{e}_{aq} to \cdot H by [2-13] is unlikely. However, a small number of \cdot H might
be available at this pH from primary events [2-8 to 2-10]. In general, the following reaction of \cdot H with SH⁻ is suggested:

$$SH^{-} + 2 \cdot H \longrightarrow H_2 S + H^{-} \dots [5-39]$$

At pH 12.7 this reaction does not occur (59, 76) because of the ionization constant for H_2S . The S⁻⁻ ion can react with •H as:

On the other hand, 'H inhibits the chain reaction for polysulphide formation:

$$s_n^{--} + \cdot H \longrightarrow SH^- + s_{n-1}^- \dots \dots [5-41]$$

The solvated electron reacts either with S⁻⁻ or with another \tilde{e}_{aq} . The rate constant for $\tilde{e}_{aq} + \tilde{e}_{aq}$ is known to be 4.5 ± 0.07 x 10⁹ M⁻¹ sec⁻¹ (13). Even though the rate constant for S⁻⁻ + \tilde{e}_{aq} is smaller than that for $\tilde{e}_{aq} + \tilde{e}_{aq}$, the concentration of S⁻⁻ is relatively large compared to \tilde{e}_{aq} . Thus it is quite likely that the solvated electron will react mainly with S⁻⁻. The following reactions can be considered as possible:

 $s^{-} + \bar{e}_{aq} \longrightarrow$ no reaction [5-42]





With regard to [5-44], formation of H_2S from an aq sodium sulphide solution at this pH is not likely.

Therefore, it can be concluded from scavenger experiments (Fig. 8, 11 and 13 and Table 2) that the •OH radicals formed in radiolysis of water initiated polysulphide formation.

5.2. Reaction Variables

A likely explanation for the effect of saturated oxygen on polysulphide yield is given below. The radical $\cdot HO_2$ (or O_2^-) which might be expected to be formed in oxygenated solutions is a fairly strong oxidizing agent [2-42, 2-52].

The rate constant for conversion of $\cdot H_{0}$ (or \bar{e}_{aq}) to $\cdot HO_{2}$ (or O_{2}) by O_{2} is 2 x 10^{10} M⁻¹ sec⁻¹. The form of $\cdot HO_{2}$ changes with pH. The neutral ($\cdot HO_{2}$) and basic (O_{2}) forms are generally accepted, and pKa values of 4.5 and 4.8 have been assigned the equilibrium [2-53].

Therefore, at high pH values O_2^- is generally the predominant species.

There will now be an excess of the number equivalents of oxidizing species over the number of reducing species equivalents. It would appear likely that this would result in an increase in the yield of polysulphide as was observed in the lower dose ranges.

However, a yield decrease in the higher dose range in oxygenated solutions might occur for the following reasons. Polysulphide decomposition is known to occur through oxidation of $S_n S^{--}$ with oxygen to $S_2 O_3^{--}$. For example (15), sodium disulphide oxidizes by the process:

 $2Na_2S_2 + 3O_2 \longrightarrow 2Na_2S_2O_3 \dots [5-45]$

Whether a polysulphide solution is stable or not at a given temperature is determined by HS⁻ and OH⁻. The stabilizing effect of HS⁻ is considerably larger than the counteracting OH⁻ effect (37).

On the other hand, during long irradiation, the HS⁻ is decreased as follows:

 $HS^{-} + \cdot HO_{2} \longrightarrow SO_{2}^{-} + H_{2} \dots [5-46]$ $HS^{-} + O_{2}^{-} \longrightarrow HSO_{2}^{--} \dots [5-47]$

Since equilibria of [2-5] or [5-27] could be destroyed by decreased SH⁻, the S_pS⁻⁻ yield seems to be decreased.

Since pH may determine structure of the solute and alter properties of the primary reactive species in irradiated water, changes in pH may affect to a great extent the reaction by which polysulphide is formed. As mentioned, the following pH dependent equilibria have been established (86).

- 1. For reducing species:
 - (i) in acidic solution the relatively slow association of $\cdot H$ and H^+ [2-23]; and
 - (ii) in alkaline solution the conversion of $\cdot H$ to \bar{e}_{aq} [2-23].
- 2. For oxidizing species:
 - (i) in acidic medium existence of the equilibrium

 $\cdot OH + H_3 O^+ \iff H_2 O^+ + H_2 O \dots [5-48]$

is possible but needs experimental
verification;

- (ii) in neutral medium the oxidizing radical is not charged and most likely exists in the form of •OH; and
- (iii) in alkaline solution the conversion
 of •OH to O⁻ becomes important accord ing to the equilibrium

 $\begin{array}{c} \cdot \text{OH} + \text{OH}^{-} \xrightarrow{k_{f}} \text{O}^{-} + \text{H}_{2}\text{O} \quad \dots \quad [5-49] \\ \text{where; } \text{K}_{f} = 1.2 \times 10^{10} \text{ M}^{-1} \text{ Sec}^{-1} \\ \text{K}_{b} = 9.2 \times 10^{7} \text{ M}^{-1} \text{ Sec}^{-1}; \text{ and} \\ \text{(iv)} \quad \text{in alkaline solution or neutral solution, there is dissociation of the} \\ \text{HO}_{2} \cdot \text{ radical } [2-53]. \end{array}$

Further, the O⁻ ion radical is an oxidizing species like the •OH radical but behaves quite differently in the

It is known that $G_{(Fe^{3+})}$ increases with increasing acidity (33).

when pH = 5.8, $G_{(Fe^{+3})} = 13.95$ $G_{\cdot H^{+}}\bar{e}_{aq} = 3.29$, $G_{OH} = 2.74$ when pH = 1.3, $G_{(Fe^{+3})} = 15.52$ $G_{\cdot H^{+}}\bar{e}_{aq} = 3.7$, $G_{\cdot OH} = 2.9$

It is also known that the increase in acidity induces an increase in water decomposition.

when	3 <u><</u> pH <u><</u>	13,	2	^G (-H ₂ O)	=	4.09
	G. _{H+ēaq}	= 3	.18,	G _{H2}	=	0.45,
	G.OH	= 2	.72,	^G H ₂ O ₂	=	0.68
when	рН	= 1	.3,	^G (-H ₂ 0)	=	4.36~ 4.5
	G.H+ēaq	= 3 3	.49~ .7,	G.OH	=	2.85~ 2.90,
	G _{H2} O2	= 0	.76.	G _{H2}	=	2.85

The present experimental results can be explained in the following way. Since the formation of •OH radical is highest in the neutral N_2^0 system, this system shows largest $G_{(S_nS^{--})}$ values. A chain reaction must occur in this system because $G_{(S_nS^{--})}$ exceeds $G_{(\cdot OH)} + G_{(\overline{e}_{aq})}$. The main oxidizing species is 0⁻ instead of $\cdot OH$ as found in the alkaline solution. The 0⁻ reacts much more slowly than does $\cdot OH$ in an electron transfer reaction, which is an important reaction in polysulphide formation. Therefore, in the alkaline N_2^0 system the radiation yield shows a smaller value than does that of the neutral N_2^0 system.

In the extremely acidic solution (pH 1.0), the G-value was the smallest of any of the N₂O systems. The \cdot H₍is the main reducing species in acidic solution. The electron scavenger N₂O can transform \bar{e}_{aq} into \cdot OH, but it can not react with \cdot H atoms [2-32, 2-33] and:

 \cdot H + N₂O \longrightarrow no reaction [5-50]

Therefore, the effect of N_2^{0} on polysulphide formation in acidic solutions is negligible. The unreacted $\cdot H$ thus inhibits polysulphide formation by chain reaction through formation of HS^{-} .

The smaller G-value obtained in the alkaline 2-propanol system has already been discussed.

A slightly higher G-value shows in the acidic 2-propanol system than in the alkaline 2-propanol system. This is believed to be due to an increase in water decomposition by radiolysis

with increasing acidity.

The effects of changes in solute concentration upon radiation yield are illustrated in Fig. 7, 16, 17 and Table 2.

As noted, in aq Na₂S solution the equilibria have been established as [5-2] and [5-16]. The SH⁻ and OH⁻ ions then react with S₀ to form polysulphide as a general chemical preparatory method [5-27]. For low Na₂S concentrations, since there is less chance for recombination of S⁻ to S_nS⁻⁻, the polysulphide yield should be small. Therefore, the degree of polysulphide formation is dependent on sulphide concentration. Baker (15) has already mentioned that the degree of oxidation to polysulphide with MnO₂ is dependent on sulphide concentration:

 $Na_2S + MnO_2 + H_2O \iff S_0 + 2NaOH + MnO \dots$ [5-51] (n-1) $S_0 + Na_2S \iff Na_2S_n \dots$ [5-52]

The influence of direct radiation effects on polysulphide formation is not suggested because yield of polysulphide was not much higher for 80 g/l aq solutions than for 40 g/l solutions (Fig. 16, 17 and Table 2). However, if a direct effect could be considered at these higher concentrations, the chemical transformation in a solute due to energy deposition directly in the solute would become important and could be explained as follows.

In concentrated solutions the major energy deposition

would still be with water components providing only "indirect effects". Assuming, as a working approximation, that these modes of radiolysis are independent, then the overall decomposition may be described by the linear relation:

$$^{G}(s_{n}s^{--}) = ^{G}(s_{n}s^{--})_{H_{2}O} + ^{G}(s_{n}s^{--})_{SH} - \cdots$$
 [5-53]

Here $G_{(S_nS^{--})_{H_2O}}$ signifies the coefficient of net

polysulphide formation by the "indirect effects" and $G_{(S_nS^{-2})_{SH}}$ the coefficient for polysulphide formation from S^{-} by "direct effects". The determination of these indirect and direct effects at higher concentration is not easy.

At higher concentrations, a direct action may be significant due to interference with spur and track reactions, and there is some evidence that H_2O^* molecules or subexcitation may transfer energy directly to the solute (32, 86).

Hydrogen sulphide has an important effect on yield increase in polysulphide formation. Packer (76) proposed that H_2S disappeared in the radiolysis of aq H_2S solutions through its interaction with reactive species like \cdot OH and \cdot H. Polysulphide was produced as shown in the series [2-67 to 2-69, 5-19 and 5-23].

The oxidation of hydrogen sulphide to \cdot S may be attributed (76) to [2-67 and 5-18]. The overall reaction is:

 $H_2S + 2 \cdot OH \longrightarrow S + 2H_2O \dots [5-54]$

The alternative, as shown in the preliminary experimental report (99), is that aq Na_2S solution can be acidified by H_2S . This can be explained by progressive $\cdot OH$ radical oxidation of H_2S to SO_4^{--} (61). In the present work it is difficult to distinguish between this particular series of reactions and other alternatives which would result in the same overall reaction. For example [2-16] and:

By a similar sequence, the addition of an \cdot OH radical is followed by \cdot H abstraction by another \cdot OH radical; the H₂SO₂ might be converted to sulphate. The overall reaction is:

 $H_2S + 8 \cdot OH \longrightarrow SO_4^{--} + 4H_2O + 2H^+$. [5-57]

Chiu (23) suggested that the apparent Na_2S degradation yield $G_{(-Na_2S)}$ in aqueous solution is pH dependent. His values of $G_{(-Na_2S)}$ ranged between 5.0 for a solution at pH 12.5 to 7.5 at pH 8.4. The yield of polysulphide excess sulphur $G_{(S_nS^{--})}$ was also shown to be pH dependent. At initial pH = 8.38

 $G_{(S_nS^{--})} = 1.1$

 $G_{(-Na_2S)} = 7.5$

At initial pH = 12.46

 $G_{(S_nS^{--})} = 0.1$ $G_{(-Na_2S)} = 5.0$

The Na₂S - H₂S system gave considerably higher yields of S_nS^{--} (Fig. 7, 14, 16 and 17 and Table 2). This may be due to an increase in S^{--} concentration by the H₂S gas treatment. Thus changes in pH by using H₂S in the sulphide solution would result in both an increase in, and a change in nature of, the intermediates. This is especially true with regard to oxidizing species formed in water radiolysis, as noted in the previous section. These will have important effects in polysulphide formation.

Response to the dose effect was generally found to increase linearly only in the lower dose range. Experimental results beyond the initial dose range with O₂ addition showed that polysulphide decreased with further irradiation up to 20 Mrad. This is not unusual in radiation chemistry. However, most treatments gave increased polysulphide yields as dose increased, even beyond the dose range used for G-value calculations (Fig. 7, 8, 11 to 14 and 17). A likely explanation for this pheomenon is occurrence of S_0 in the radiolysis of sulphur containing compounds at later irradiation stages as mentioned. This S_0 would appear to initiate a polysulphide chain reaction. As suggested by Abellan (1), with regard to radiolysis of aq $Na_2S_2O_3$, the presence of S_0 was noticed only at higher doses. On the other hand, organic impurities could also be responsible for these spurious results.

6.0. RECOMMENDATIONS

(1) Detailed estimation of radiolysis products, i.e., OH and SH, in the generated polysulphide solution would be of value in establishing stoichiometric relationships for the polysulphide reaction.

(2) A study of radiolytic generation of polysulphide in O_2 saturated aq Na_2S solutions should be attempted in order to observe effects of O_2 at higher doses on radiation products. The effect of oxygen on polysulphide formation showed marked fluctuation of G-values at higher doses, suggesting depolyminization.

(3) Some other stable \overline{e}_{aq} scavengers should be tried for promotion of polysulphide yield.

(4) Effect of dose rate or intensity on polysulphide formation should be studied.

(5) Overall kinetics should be studied with respect to especially •OH propagation and termination steps.

(6) Further studies on variation of parameters defined at higher dose could help elucidate factors critical to optimum polysulphide yields. This area of research could have commercial importance if suitable systems are found.

The following general conclusions may be drawn from this study:

(1) Polysulphide can be formed from aq Na_2S solution by γ -radiation.

(2) Polysulphide is thought to be formed indirectly through action of oxidizing intermediates available in irradiated aqueous solutions.

(3) The polysulphide yield varied according to several factors including dosage, presence of N_2^{0} , pH of the solution, presence of S⁻⁻ and H₂S, and whether O_2 was present. Thus the yield affecting factors may be considered as follows:

- (i) polysulphide yield was almost linearly proportional to dosage;
- (ii) use of N₂O as an electron scavenger was found to efficiently increase polysulphide yield,
- (iii) pH had a great effect on polysulphide formation, wherein a neutral solution is recommended to produce the highest yield;
- (iv) concentration of dissolved Na₂S had considerable affect on yield,
- (v) H₂S over-pressure considerably increased yield; and
- (vi) O₂ was found to have strong effects only during early stages of irradiation.

(4) Commercial application of the method for polysulphide generation is limited by excessively high dose requirements needed to obtain solutions of suitable strength. The present study sorted out certain basics of radical species activity and related these to polysulphide formation reactions,
but did not describe conditions maximizing polysulphide yields
within economic boundaries.

8.0. LITERATURE CITED

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Table 1.

Reactions of free radicals in irradiated water (33).

Reaction $M^{-1} \sec^{-1}$ pH $c_{aq}^- + c_{eq}^ 2^{1120}$ $H_2 + 20H^ 5.5 \times 10^9$ 13.3 $s_{aq}^- + e_{eq}^ H_2 + 20H^ 5.5 \times 10^9$ $10-13$ $e_{aq}^- + H$ $H_{20}^ H_2 + 0H^ 2.5 \times 10^{10}$ 10.5 $e_{aq}^- + H$ $H_{20}^ H_2 + 0H^ 2.5 \times 10^{10}$ 10.5 $e_{aq}^- + 0H$ $OH^ 3.0 \times 10^{10}$ 11 $e_{aq}^- + O^ 20H^ 2.2 \times 10^{10}$ 13 $e_{aq}^- + H_3O^+$ $H + H_2O$ 2.06×10^{10} $2.1-4.3$ 2.36×10^{10} $4-5$ 2.2×10^{10} $ 2.2 \times 10^{10}$ $ 2.2 \times 10^{10}$ $-$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$
$e_{ac}^{c1} + H_{3}O^{+} \longrightarrow H + H_{2}O$ 2.06 × 10 ¹⁰ 2.1-4.3 2.36 × 10 ¹⁰ 4-5 2.2 × 10 ¹⁰ - 2.6 × 10 ¹⁹ 4-5
$\begin{array}{cccccccccccccccccccccccccccccccccccc$
2.2×10^{10}
2.26×10^{19} $4.1 - 4.7$
2.20 × 10
$\mathbf{e}_{33}^- + \mathbf{H}_2\mathbf{O}_2 \longrightarrow \mathbf{OH} + \mathbf{OH}^- 1.23 \times 10^{10} 7$
1.36×10^{10} 11
1.1×10^{10} —
1.3×10^{10} 11
$c_{3q}^- + HO_2^- \longrightarrow O^- + OH^- \qquad 3.5 \times 10^9 \qquad 13$
$e_{z_0}^- + H_2O \longrightarrow H + OH^-$ 16 8.3-9.0
$H + H \longrightarrow H_2$ 1.5×10^{10} $0.2-0.8 N H_2 SO_1$
1.0×10^{10} 2.1
7.75×10^9 3
1.3×10^{10} 0.4–3
1.25×10^{10} 2-3
$H + OH \longrightarrow H_2O$ 3.2×10^{10} $0.4-3$
$H + OH^- \longrightarrow e_{aq}^ 1.8 \times 10^7$ 11.5
2.2×10^7 11-13
$H + H_2O_2 \longrightarrow H_2O + OH$ 5×10^7 acid
1.6×10^8 0.4-3
9×10^{7} 2
4×10^7 —
$OH + OH \longrightarrow H_2O_2$ 6×10^9 $0.4-3$
4×10^{9} 7
5 × 10°
$0 + 0 \longrightarrow 0_{\tilde{2}}$
$\xrightarrow{H_2O} HO_2^- + OH^- \qquad 1 \times 10^9 \qquad 13$
$OH + OH^- \longrightarrow O^- + H_2O$ $3.6 \times 10^8 \longrightarrow$
$OH + H_2O_2 \longrightarrow HO_2 + H_2O \qquad 4.5 \times 10^7 \qquad 7$
1.2×10^7 0.4–3
2.25×10^{7} —
$O^- + HO_2^- \longrightarrow O_2^- + OH^- \qquad 7 \times 10^8 \qquad 13$
2.74×10^{8} 13
$O(1 + 1), \longrightarrow 1(+1), O = 6 \times 10^7$ 7
4.5×10^7 7
$O^- + H_2 \longrightarrow H + OH^- 8 \times 10^7$ 13
$H_3O^+ + OH^- \longrightarrow 2H_2O$ 14.3×10^{10} -
15×10^{10} —
$4.4 \times 10^{10} a$ —

* Low value obtained in neutral solution with high-intensity pulses.

Na ₂ S,g/l	10					40					80
Additives(s)	N ₂ 0 ^a H ₂ S	None	N20 H2 ^{SO} 4	N ₂ O H ₂ SO ₄	N ₂ 0	2-prop. ² H ₂ SO ₄	2-prop.	H ₂ S	02 ^{ab}	N ₂ 0 H ₂ S	N20 H25
Initial pH	12.7	12.7	1.0	7.0	12.7	1.0	12.7	12.7	12.7	12.7	12.7
Dose, Mrad				· · ·	<u></u>	<u> </u>	•.				
.96	0.050	0.029	0.023	0.405	0.180	0.017	0.012	0.031	1.120	0.256	0.245
1.28	0.065	0.034	0.029	0.460	0.235	0.023	0.016	0.045	0.790	0.330	0.310
1.60	0.080	0.036	0.035	0.510	0.300	0.023	0.020	0.054	0.720	0.425	0.385
1.92	0.095	0.040	0.040	0.545	0.360	0.024	0.025	0.064	0.610	0.490	0.485
5.12	0.290	0.047	0.110	1.950	1.100	0.034	0.046	0.823	0.310	2.250	2.460
10.00	0.600	0.063	0.500	3.800	3.000	0.046	0.075	2.725	0.413	7.500	4.850
15.00	0.800	0.120	0.565	4.900	4.850	0.052	0.151	3.704	0.132	10.000	9.000
20.00	2.200	0.340	0.625	6.100	6.150	0.068	0.340	8.324	0.151	10.500	14.000
G(S _n S)	1.35 ±0.20	0.75 ±0.01	0.63 ±0.01	10.06 ±1.00	5.79 ±0.60	0.53 ±0.01	0.39 ±0.01	1.04 ±0.10	108.30 ± 5.00	7.23 ±0.70	7.84 ±0.80
Fig.	7	8	9	10	11	12	· 13	14	15	16	17

Table 2. Radiolytic generation of sodium polysulphide (g/l) as related to sodium sulphide concentration, additive(s), initial pH and radiation dose.

^a N₂O, H₂S and O₂ maintained at 20 psi; 2-propanol at 0.5 M.



Fig. 1. Variation with pH of primary yields in γirradiated water (86).



Fig. 2. Dependence of primary radical and molecular yields of water γ-radiolysis on pH, derived from measurements on formic acid-oxygen solutions (33).



Fig. 3. Stainless steel high pressure cell and glass diffusion tube in cut-off Erlenmeyer flask.

Gas Traps



Fig. 4. Schematic Diagram of the Pressurized System.











Fig. 7. Polysulphide yield related to radiation dose for 10 g/l aq Na_2S , N_2O (20 psi) and H_2S (20 psi); initial pH 12.7.



Fig. 8. Polysulphide yield related to radiation dose for 40 g/l aq Na₂S and no additives; initial pH 12.7.



Fig. 9. Polysulphide yield related to radiation dose for 40 g/l aq Na₂S and N₂O (20 psi); initial pH 1.0.



Fig. 10. Polysulphide yield related to radiation dose for 40 g/l aq Na₂S and N₂O (20 psi); initial pH 7.0.



Dose, Mrad

Fig. 11. Polysulphide yield related to radiation dose for 40 g/l aq Na₂S and N₂O (20 psi); initial pH 12.7.



Fig. 12. Polysulphide yield related to radiation dose for 40 g/l aq Na₂S and 2-propanol (0.5 M); initial pH 1.0.



Fig. 13. Polysulphide yield related to radiation dose for 40 g/l aq Na₂S and 2-propanol (0.5M); initial pH 12.7.


Fig. 14. Polysulphide yield related to radiation dose for 40 g/l aq Na₂S and H₂S (20 psi); initial pH 12.7.



Fig. 15. Polysulphide yield related to radiation dose for 40 g/l aq Na₂S and O₂ (20 psi); initial pH 12.7.





Fig. 16. Polysulphide yield related to radiation dose
for 40 g/l aq Na₂S, N₂O (20 psi) and H₂S
(20 psi); initial pH 12.7.



Fig. 17. Polysulphide yield related to radiation dose
for 80 g/l aq Na₂S, N₂O (20 psi) and H₂S
(20 psi); initial pH 12.7.