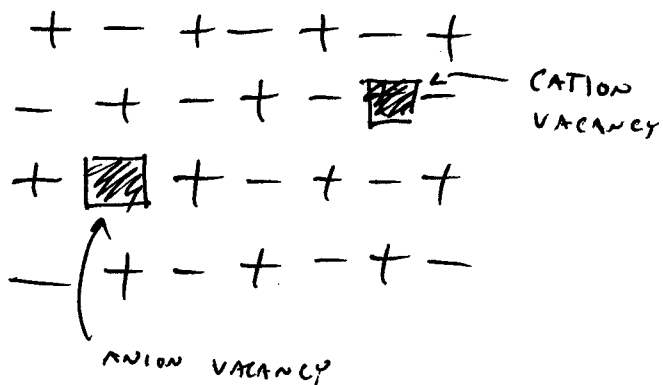
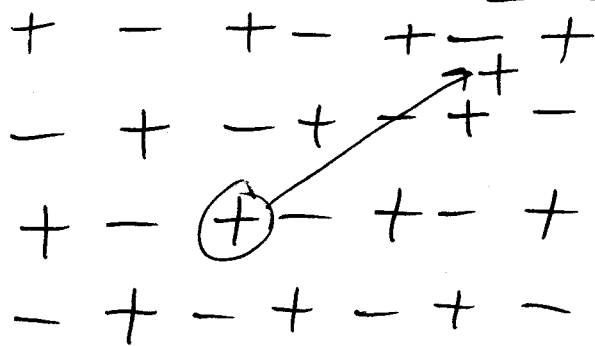


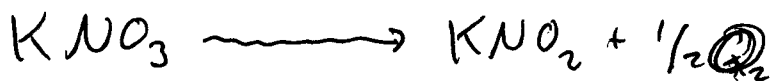
# RADIATION + MATTER PT 2

11

## NaCl



INORGANIC SUBSTANCES EXPOSED TO HIGH  $\gamma$ -RAY FLUENCES EXPERIENCE DECOMPOSITION



AFTER HIGH ENOUGH OXYGEN CONCENTRATION THE PRESSURE WILL CAUSE THE CRYSTAL TO SHATTER.

THEORY HAS NOT BEEN DEVELOPED SUFFICIENTLY TO ALLOW QUANTITATIVE CALCULATION OF THE RADIATION SENSITIVITY OF COMPOUNDS

- EMPIRICALLY IT HAS BEEN FOUND THAT COVALENT BINARY COMPOUNDS ARE HIGHLY RADIATION RESISTANT.
- THIS IS WHY  $UO_2$  &  $UC$  WHOSE INSENSITIVITY TO RADIATION HAS LEAD TO THEIR USE IN NUCLEAR REACTOR FUELS.

# FUEL ELEMENTS IN WATER-COOLED REACTORS

UO<sub>2</sub> IS USED IN THE FORM OF 1 cm<sup>3</sup> PELLETS.

↳ FISSION GAS BUILDUP PRESSURE LEADS TO CRACKING.  $\geq 10^{22}$  n/cm<sup>2</sup>

- MIXTURES OF INORGANIC COMPOUNDS LEAD TO UNEXPECTED & UNDESIRABLE REACTIONS.

RADIOLYSIS OF LIQUID AIR / GASEOUS AIR → OZONE

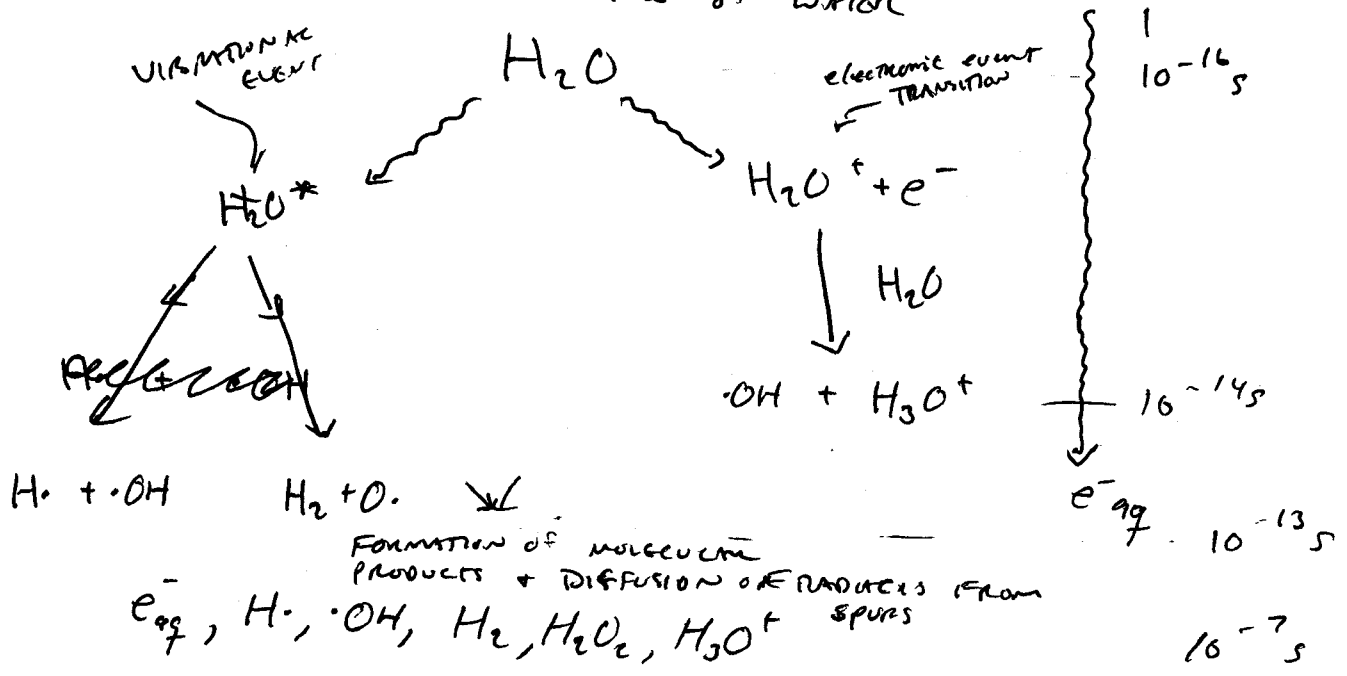
HUMID AIR

- N 78%
- O 21%
- Ar 1%
- + - H<sub>2</sub>O -

→ HNO<sub>3</sub>

PHASES OF IRRADIATION

## TIME SCALE OF RADIOLYSIS OF WATER



ONE OF THE FIRST OBSERVATIONS OF RADIATION-INDUCED CHANGE WAS DARKENING OF GLASS

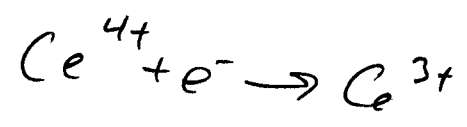
→ GLASS CONTAINS IRON, MANGANESE, & OTHER METALS THAT CAN EXIST IN SEVERAL OXIDATION STATES, WITH DIFFERENT COLORS.

→ (RADIATION CAUSES THE OXIDATION STATE TO CHANGE, CHANGING COLOR.

DISLOCATIONS AS WELL AS TRAPPED ELECTRONS CONTRIBUTE TO COLOR CHANGE.

ON A PRACTICAL NOTE, IT IS DESIRABLE TO OBSERVE EXPERIMENTS WHILE BEING IRRADIATED, HOT CELLS, ACCELERATOR DIAGNOSTICS, ETC.

IN ORDER TO AVOID COLORING, A SMALL AMOUNT OF AN ELEMENT IS ADDED WHICH ACTS AS AN ELECTRON TRAP. CeO<sub>2</sub> FOR INSTANCE



10<sup>4</sup> Gy ORDINARY GLASS TRANSMISSION @ 44%  
CeO<sub>2</sub> PROTECTED GLASS, 89%

GLASS IS VERY RESISTANT TO RADIATION DAMAGE

BECAUSE IT IS NOT CRYSTALLINE, BUT RATHER A SOLID LIQUID.

→ IT IS NOT POSSIBLE TO SPEAK OF DISLOCATIONS,

RANDOM STRUCTURE OF GLASS HAPPILY ACCEPTS ~~PERMANENT~~ FOREIGN SPECIES THROUGHOUT THE BULK.

PERFECT "CONTAINER" FOR HIGH ACTIVITY WASTE OF FISSION PRODUCTS & ACTINIDES!

- POTENTIAL GUEST LECTURE A

- CONSEQUENCES OF IONIZATION + EXCITATION DEPEND ON THE PHYSICAL STATE + MOLECULAR COMPOSITION OF THE IRRADIATED MATERIAL.

TIME SEQUENCE:

EMPA

- IONIZATION EVENT OCCURS ON TIME SCALE OF  $10^{-16}$  s
- POSITIVE ION  $H_2O^+$  FORMED REACTS WITH WATER  $\sim 10^{-14}$  s  $\rightarrow$  FORMING  $\cdot OH$  RADICAL +  $H_3O^+$

(THE  $e^-$  IF LIBERATED WITH ENOUGH ENERGY CAN CAUSE FURTHER IONIZATION UNTIL IT FALLS BELOW 12.61 eV)

$\hookrightarrow$  REST OF  $e^-$  IS LOST BY VIBRATION + ROTATIONAL EXCITATION,

FINALAY IT BECOMES SOLVATED....

- SOLVATION PROCESS OCCURS WITHIN  $10^{12}$  s
- EXCITED STATES DISSOCIATE WITHIN  $10^{-14} \rightarrow 10^{-13}$  s
- ~~THESE~~  $\hookrightarrow$  SAME TIME SCALE MOLECULAR VIBRATION TO FOR  $O\cdot$ ,  $H\cdot$ ,  $\cdot OH$  +  $H_2$
- RADIOLYSIS PRODUCTS ARE CLUSTERED IN THE SPURS, + ~~CALL~~ ARE INITIALLY INHOMOGENOUSLY DISTRIBUTED IN THE WATER

→ PROCEED TO DIFFUSE OUT OF THE

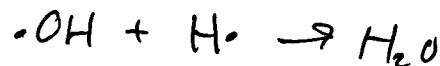
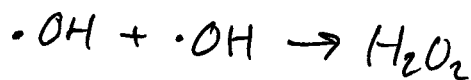
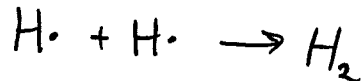
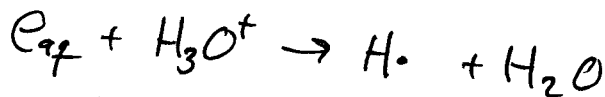
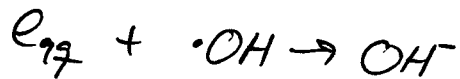
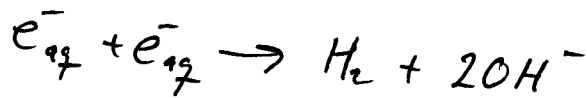
SPUR VOLUME.

↳ DURING WHICH RECOMBINATION REACTIONS TAKE PLACE, FORMING

- MOLECULAR OR
- SECONDARY RADICAL PRODUCTS.

SPUR EXPANSION IS COMPLETE WITHIN  $10^{-7}$  s

POSSIBLE SPUR REACTIONS IN WATER:



FOR GIVEN SPUR REACTIONS

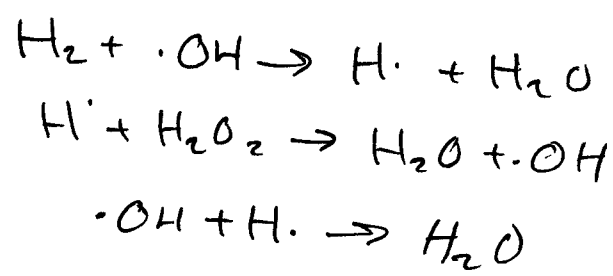
G-VALUES FOR RADIOLYSIS PRODUCTS IN WATER VARY WITH TYPES OF RADIATION

- AS L.E.T. INCREASES G-VALUES OF RADICAL PRODUCTS DECREASE
  - AS LET INCREASES, <sup>MOLECULAR</sup> G-VALUES ~~DE~~ INCREASE
- ↳ FORMATION OF TRACKS.

MOLECULAR PRODUCT FORMATION IN IRRADIATED WATER VAPOR SHOWS SPUR FORMATION + REACTIONS ARE IN SIGNIFICANT IN VAPOR  
 → TO BE EXPECTED.

ABSENT OF SOLUTES, REACTIONS BETWEEN RADICAL & MOLECULAR SPECIES OCCUR IN THE BULK WATER

EX: PURE IRRADIATED WATER BY X-RAYS, γ-RAYS (LOW LET)



NO NET DECOMPOSITION

HIGH LET IRRADIATION CAUSES DECOMPOSITION. 6/

YIELD DEPENDS ON ACIDITY...

SHOW FIG 7.6

• REACTORS COOLED BY WATER NEED REALLY PURE WATER TO MINIMIZE DISSOCIATION.

↳ AVOID FORMATION OF  $H_2$  +  $O_2$  GAS MIXTURE  
EXPLOSIVE?

• FURTHER, DECOMPOSITION PRODUCTS CAN INCREASE CORROSION OF FUEL, STRUCTURE etc

USE OF N GAS IS COMMON, BUT CAN FORM  $HNO_3$ .

↳ MITIGATION CAN ~~BE~~ IS ACCOMPLISHED FROM EXCESS  $H_2$  WHICH THEN PREFERENTIALLY YIELDS  $NH_3$

pH



# ORGANIC COMPOUNDS

7/

TWO PROPERTIES, DIELECTRIC CONSTANT  $\epsilon$  &  $e^-$  MOBILITY ARE GREAT IMPORTANCE TO THE FATE OF ION PAIRS FORMED.

THE DISTANCE  $r_c$  (ONSET RADIUS) IS THE DISTANCE AN ION-PAIR CORRESPONDS TO THERMAL ENERGY  $kT$

$$r_c = e^2 / 4\pi \epsilon_0 \epsilon_r kT$$

PERMITTIVITY OF FREE SPACE  
PERMITTIVITY OF MEDIUM

THE PROBABILITY OF AN  $e^-$  ESCAPING ITS POSITIVE ION TO BECOME A FREE ION IS EQUAL TO  $e^{-r_c/r}$

$r_c$   $\equiv$  DISTANCE  $e^-$  TRAVELS BEFORE IT BECOMES THERMALIZED.

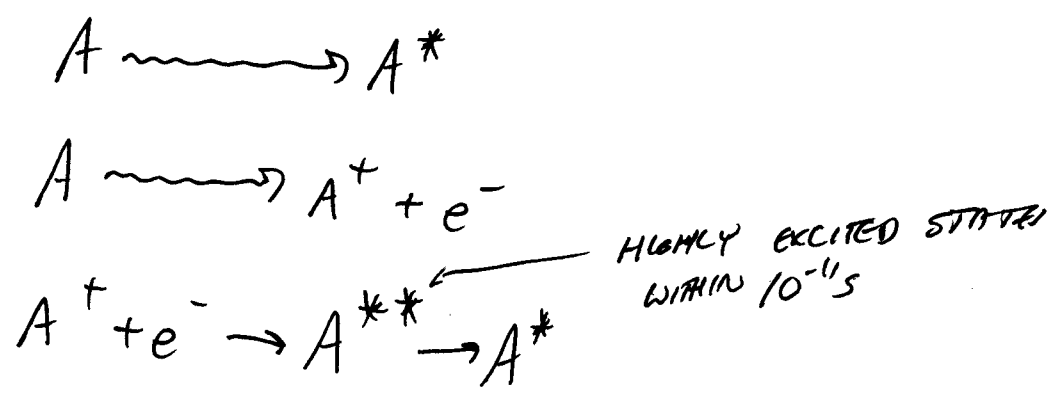
WHICH DEPENDS ON  $e^-$  MOBILITY IN MEDIUM.

MOST ORGANIC LIQUIDS HAVE A LOWER DIELECTRIC CONSTANT THAN THAT OF WATER & FREE ION YIELDS ARE GENERALLY LOWER

$e^-$  ESCAPING THEIR POSITIVE IONS ARE GRADUALLY THERMALIZED + SOLVATED

$e^-$  THAT RECOMBINE WITH THEIR GEMINATE (ORIGINAL ION PAIR) RADICAL CATIONS, FORM EXCITED MOLECULES

→ RADICAL CATIONS MAY REACT WITH SOLVENT MOLECULES SUCH AS PROTON, HYDROGEN ATOM, HYDRIDE ION X-FER



~~HIGHLY EXCITED STATES CAN RETURN TO THEIR GROUND~~

HIGHLY EXCITED, (ELECTRONICALLY AND/OR VIBRATIONALLY) MOLECULE

$A^{**}$  FORMED BY CHARGE RECOMBINATION MAY ( $10^{-11}$ s)

LOSE PART OF ITS ENERGY RAPIDLY THROUGH COLLISIONS WITH NEIGHBORING MOLECULES.

SEVERAL PROCESSES FOR WHICH THE EXCITED MOLECULES CAN RETURN TO GROUND STATE.

SINGLET STATES (ANTI-PARALLEL SPINS OF VALENCE  $e^-$ )  
DE-EXCITE WITHIN  $10^{-8}$  S BY FLUORESCENCE

TRIPLET STATES PARALLEL SPINS OF OUTER  $e^-$   
DE-EXCITE  $\sim 10^{-5} \rightarrow 10$  SEC PHOSPHORESCENCE

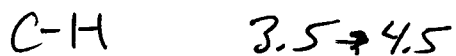
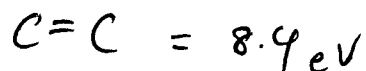
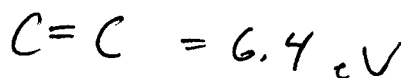
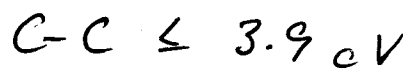
ALTERNATIVELY, THE EXCITED ~~STATE~~ MOLECULES CAN UNDER GO MOLECULAR ISOMERIZATION OR DISSOCIATE INTO HIGHLY REACTIVE RADICALS

ORGANIC MOLECULES HAVE MORE ATOMS THAN WATER,  
THUS A GREATER VARIETY OF PRODUCTS WILL RESULT.  
BOTH  
 $\rightarrow$  SMALLER + POLYMERIC MOLECULES

# RADIATION EFFECTS ON ORGANIC MOLECULES

STRONGLY DEPENDANT ON MOLECULAR STRUCTURE,

SINCE EXCITATION ENERGY IS RAPIDLY SPREAD OUT OVER WHOLE MOLECULE, ONE WOULD EXPECT WEAKEST BOND TO RUPTURE, PRODUCING TWO RADICALS PROVIDED ENERGY EXCEED BOND ENERGY

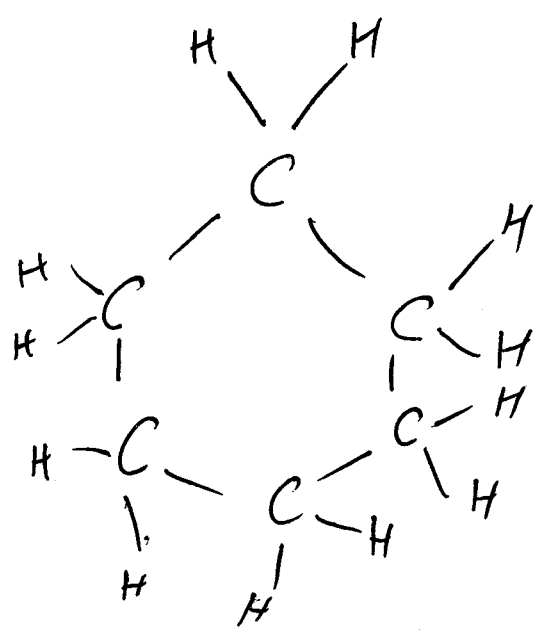


ALTHOUGH C-C BONDS ARE WEAKER THAN C-H BONDS

C-H RUPTURE PRE-DOMINATES

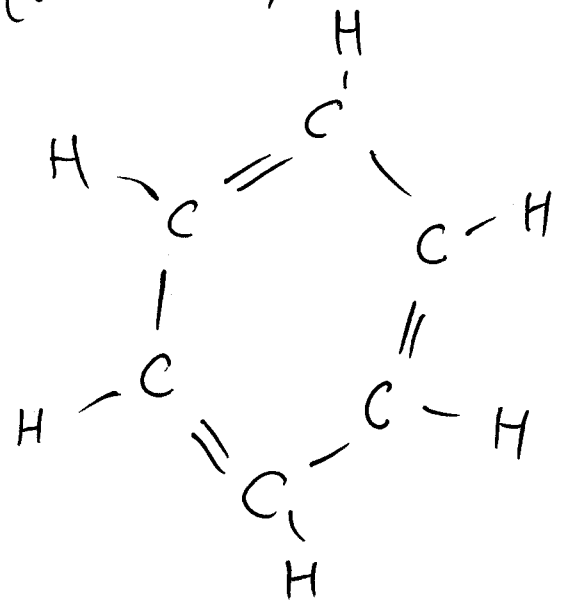
$^{60}\text{Co}$   $\gamma$ -RAY IRRADIATION Hydrogen Yield from Cyclohexane IS 150X Greater than that of BENZENE

COMPOUNDS WITH UNSATURATED BONDS ARE MORE RADIATION RESISTANT THAN THOSE WITH SATURATED BONDS



CYCLOHEXANE  
SATURATED BOND

BENZENE (UNSATURATED, CONTAINS AT LEAST 1 - C=C DOUBLE BOND)



# $\gamma$ - RADIATION ON A FEW TECHNICALLY USED ORGANIC COMPOUNDS

OILS  $\rightarrow$  CHANGES ARE MAINLY VISCOSITY + ACIDITY

PLASTICS  $\rightarrow$  FORMATION OR RUPTURE OF CROSS-LINKING.

ELASTOMERS. (RUBBERS), CHANGE IN ELASTICITY

## POLYETHYLENE

- 10  $\rightarrow$  100 kGy TENSILE STRENGTH INCREASE
- 100  $\rightarrow$  2000 kGy BECAME LIKE JELLY / RUBBER
- 2000  $\rightarrow$  5000 kGy BECAME HARD
- > 5000 kGy BECAME GLASSY W/ HIGH ELASTICITY

STOP.

SOLUTES IN LOW CONCENTRATION IN ORGANIC SOLVENTS  
REACT PRIMARILY WITH RADICALS FORMED