

**Introduction to Advanced Oxidation Processes (AOPs) and Photochemical Based AOPs**

*James Bolton (U of A, Edmonton, Canada)  
and  
Thomas Oppenländer  
Hochschule Furtwangen University, Germany  
Department of Process Engineering*

---

---

---

---

---

---

---

---

**Outline**

- Definitions
- Survey: Advanced Oxidation Technologies
- The Hydroxyl Radical
- AOT Mechanism
- Basics of Photochemistry
- UV Treatment of NDMA
- Development Status of Photochemical AOTs
- Organic Parameters of Water Analysis

---

---

---

---

---

---

---

---

**Some important definitions**

- **AOP: Advanced Oxidation Process**
- **AOT: Advanced Oxidation Technology**
- **UV: ultraviolet radiation**
- **VUV: vacuum-UV radiation between 100 nm and 200 nm**

---

---

---

---

---

---

---

---

### Advanced Oxidation Technologies (AOTs)

- Usually involve the generation of hydroxyl radicals ( $\bullet\text{OH}$ ).
- Called "Advanced" because the reactions are just highly accelerated oxidation reactions that occur when pollutants enter the environment.
- The  $\bullet\text{OH}$  radicals react with organic pollutants to initiate a series of oxidative degradation reactions.
- The overall process often leads to mineralization (i.e., conversion to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and mineral acids) of the pollutants.

---

---

---

---

---

---

---

---

### Survey of Advanced Oxidation Processes (AOPs)

---

---

---

---

---

---

---

---

### The Hydroxyl Radical

---

---

---

---

---

---

---

---

### The Hydroxyl Radical

- Reacts (usually with very high rate constants) by
  - hydrogen abstraction (saturated aliphatics)
  - addition to double bonds (unsaturated & aromatics)
  - electron transfer (primarily with inorganics)
  - radical-radical reactions (e.g.,  $\cdot\text{OH} + \text{HO}_2\cdot$ )
- Molar absorption coefficients
  - $\epsilon_{230} = 530 \text{ M}^{-1} \text{ cm}^{-1}$ ;  $\epsilon_{260} = 370 \text{ M}^{-1} \text{ cm}^{-1}$
- $\text{pK}_a = 11.9$
- $E^\circ = 2.7 \text{ V}$  (acid solution)

---

---

---

---

---

---

---

---

### AOT mechanism

- $\cdot\text{OH}$  radicals react with organic compounds by:
  - hydrogen abstraction from aliphatic compounds
    - $\cdot\text{OH} + \text{CH}_3\text{OH} \longrightarrow \cdot\text{CH}_2\text{OH} + \text{H}_2\text{O}$
  - addition to unsaturated compounds
    - $\cdot\text{OH} + \text{CH}_2=\text{CH}_2 \longrightarrow \cdot\text{CH}_2\text{CH}_2\text{OH}$
- This is followed by reaction with oxygen initiating a series of degradative oxidation reactions

---

---

---

---

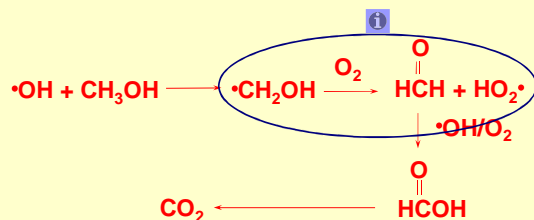
---

---

---

---

### Mechanism of methanol degradation



Other organics are more complex, but generally:  
 pollutant  $\longrightarrow$  aldehydes  $\longrightarrow$  carboxylic acids  
 $\longrightarrow$  bicarbonate

---

---

---

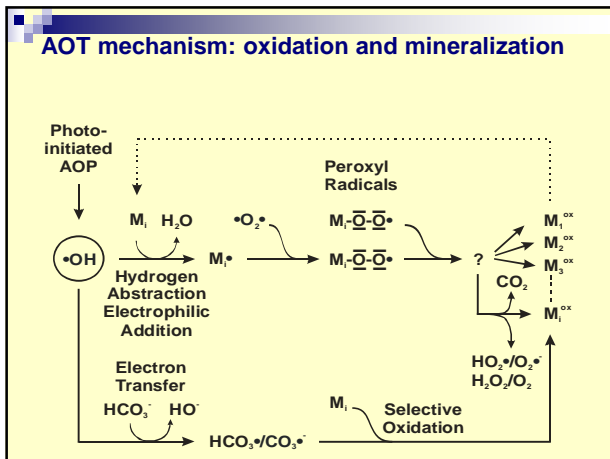
---

---

---

---

---




---

---

---

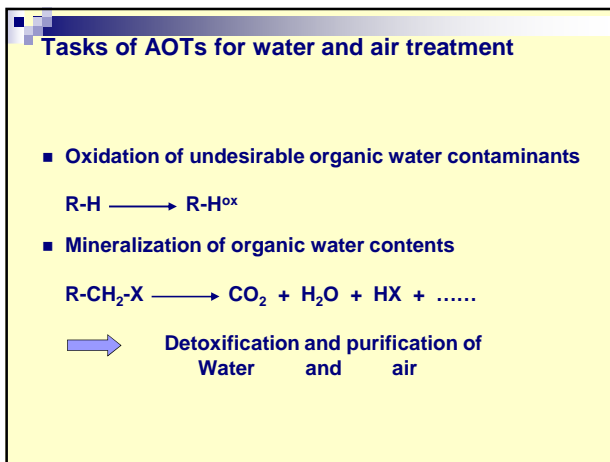
---

---

---

---

---




---

---

---

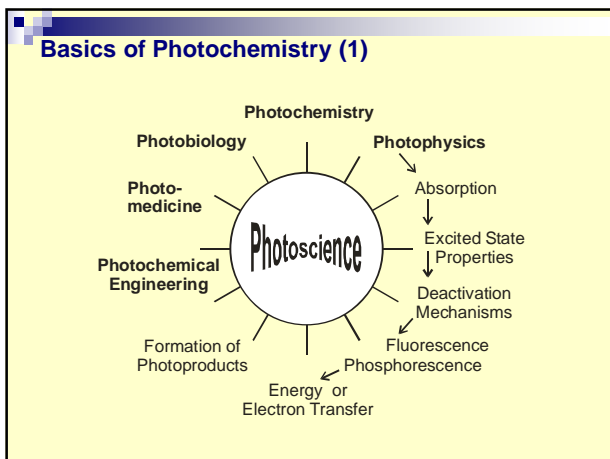
---

---

---

---

---




---

---

---

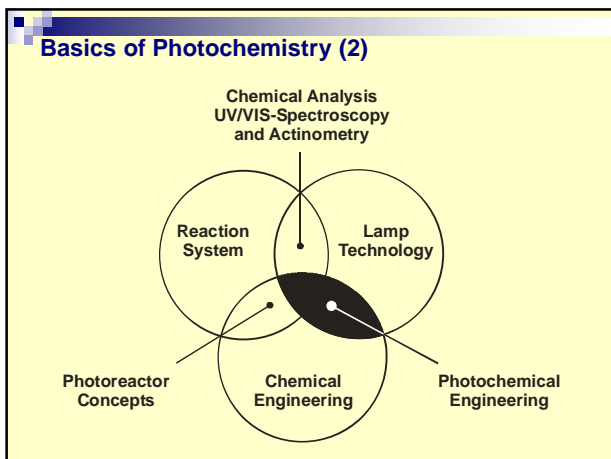
---

---

---

---

---




---

---

---

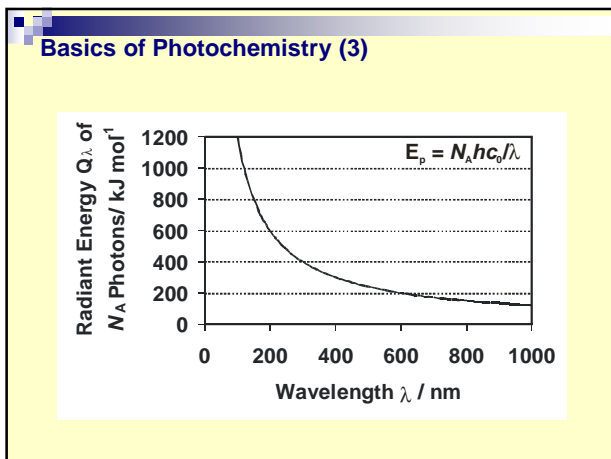
---

---

---

---

---




---

---

---

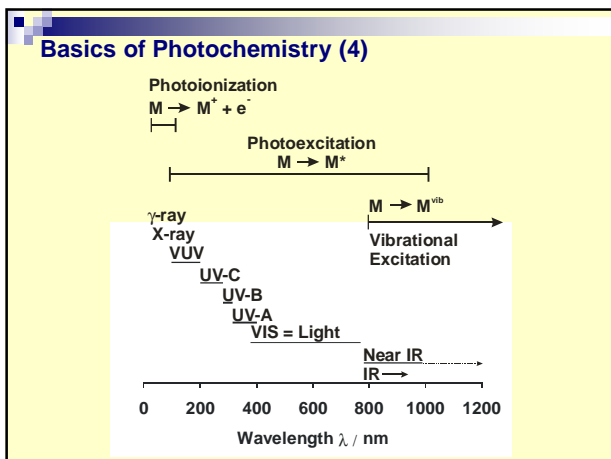
---

---

---

---

---




---

---

---

---

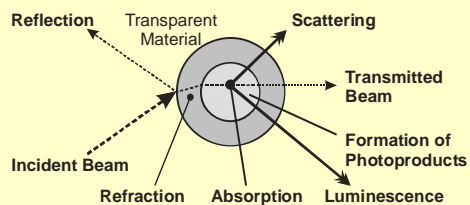
---

---

---

---

### Basics of Photochemistry (5)




---



---



---



---



---



---



---

### Basics of Photochemistry (6)

#### Rate of a Photochemical Reaction

Rate ( $R_C$ ) of photochemical reaction of component C

$$R_C = \frac{GF_C\Phi_C}{V}$$

$G$  = incident photon flow (einstein  $s^{-1}$ )

$F_C = f(\lambda)\chi_C$  = fraction of light absorbed by component C

$\Phi_C$  = quantum yield of component C

$V$  = volume (L)

---



---



---



---



---




---



---

### Basics of Photochemistry (7): Definitions

- Total fraction of light absorbed 

$$f(\lambda) = 1 - 10^{-A(\lambda)}$$

- Fraction absorbed by a single component i

$$\chi_i = \frac{\epsilon_i c_i}{a}$$

- Quantum Yield ( $\Phi_P$ )** - defined as the number of moles of product formed or reactant removed (P) per mole of photons absorbed.

$$\Phi_P = \frac{\text{moles of } P \text{ generated}}{\text{moles of photons (einsteins) absorbed}}$$

---



---



---



---



---



---



---

### Basics of Photochemistry (8): Kinetic Regimes

- If  $F_C$  is near unity, the kinetics will be “zero-order”, that is  $R_C$  will be independent of  $c_C$ .
- If  $F_C$  is  $< 0.1$ ,  $f(\lambda)$  may be expanded in a Taylor Series so that  $R_C$  reduces to:

$$R_C \approx \frac{G\Phi_C \ln(10)\epsilon_C c_C I}{V}$$

such that now the kinetics are “first-order”, that is,  $R_C$  is proportional to  $c_C$ .

---

---

---

---

---

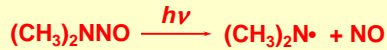
---

---

---

### Treatment of NDMA

- NDMA (N-nitrosodimethylamine) is a carcinogen that is often found in industrial effluents. It does not biodegrade, air strip or adsorb well to activated carbon. However, it does photolyze very efficiently.



- NDMA absorbs only in the range 200–250 nm; thus, a UV lamp with strong output in this region is essential for effective treatment.

---

---

---

---

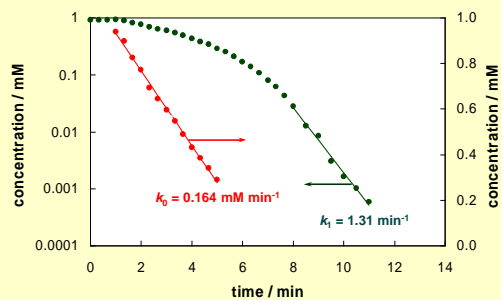
---

---

---

---

### UV Treatment of NDMA: Degradation Curves at Different Concentrations



**Question:** Which degradation curve represents zero and which first order degradation kinetics?

---

---

---

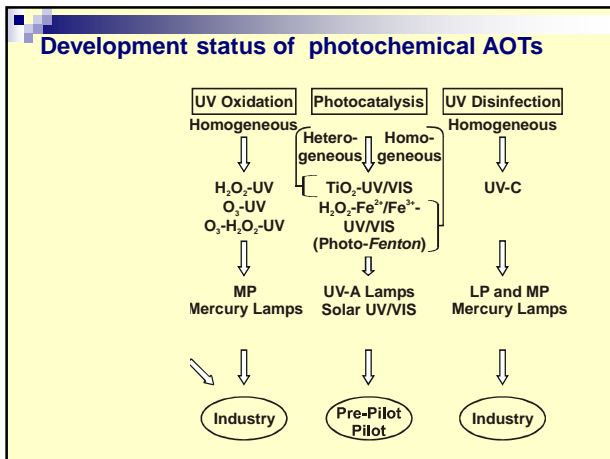
---

---

---

---

---




---

---

---

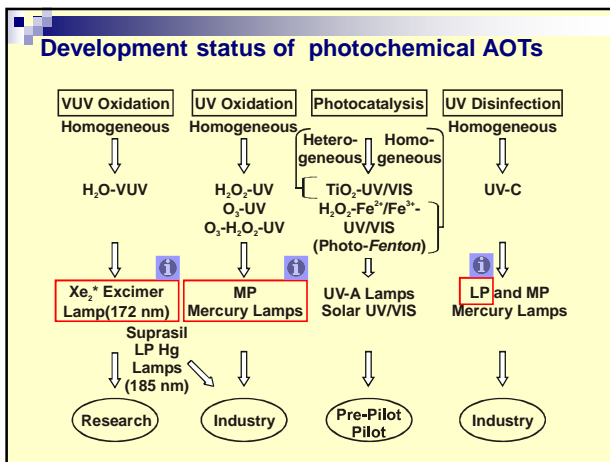
---

---

---

---

---




---

---

---

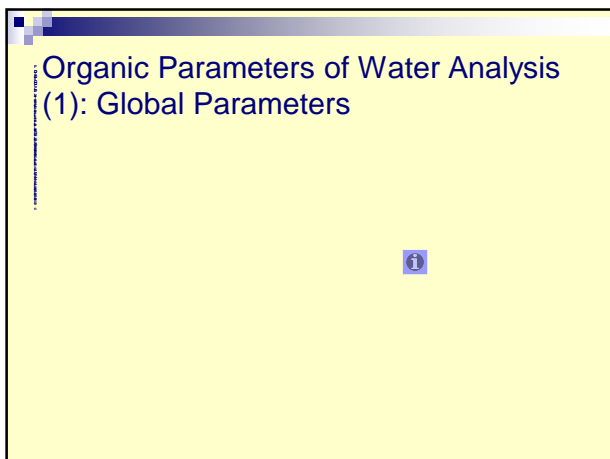
---

---

---

---

---




---

---

---

---

---

---

---

---



**Organic Parameters of Water Analysis (2):  
Group Parameters and Lead Substances**

TOX: Total Organic Halogen	Lead Substances
DOX: Dissolved Organic Halogen	NOM: Natural Organic Matter
AOX: Adsorbable Organic Halogen	HC: Hydrocarbons
EOX: Extractable Organic Halogen	PAH: Polycyclic Aromatic HCs
POX: Purgable Organic Halogen	Phenols
VOX: Volatile Organic Halogen	Chlorophenols etc.

---

---

---

---

---

---

---

---

**Hyperlinks >>>>**

---

---

---

---


---

---

---

---

**Measurement of TOC with a TOC analyzer with auto sampling unit**  
Combustion of the probe at a catalyst surface and quantification of CO<sub>2</sub>



---

---

---

---

---

---

---

---

## Second Order Rate Constants of OH-Radical Reactions with different Substrates:

Typical elementary reaction ?

Substrate +  $\cdot\text{OH} \rightarrow \text{Product}$

$$\text{Rate}_{(-\text{substrate})} = -k \cdot [\text{OH}, \text{M}] [\text{Substrate}]$$

---

---

---

---

---

---

---

---

## Examples of Second Order Rate Constants of OH-Radical Reactions with different Substrates: rate = - k · [OH, M] [Substrate]

Free Database:  
<http://kinetics.nist.gov/solution/>

---

---

---

---

---

---

---

---

NDRL/NIST  
Solution Kinetics Database  
Resources

Feedback  
Rate Out  
Products and Services  
Project status

**NDRL/NIST Solution Kinetics Database on the Web**  
NIST Standard Reference Database 40  
A compilation of kinetics data on solution-phase reactions

**Solution Database Search Form**  
Enter the reactant(s), product(s), and/or solvent(s) in the fields below. Compounds may be entered by formula, name, or CAS number. Multiply-charged species must be entered with the charge specified in the format (+/-)[number]. For example,  $\text{SO}_3^{2-}$  is entered as SO3-2. Fields may be left blank. Press the submit button to start the search. Additional help is available.

Reactants:   
Products:   
Solvents:   
 Don't return protonated/deprotonated forms or ions of input molecules

**Bibliography Search Form**  
Fill out one or more of the fields below and press the submit button to start the search.

Title:  Author(s):   
Journal:  Volume:   
Year:  Squib:

Single Oxygen  
Quantum  
Yields  
Reduction  
Potentials  
Rate constants for opening of metal complexes  
Triplet-triplet  
absorption  
spectra

NDRL/NIST  
A quick introduction to the database.

---

---

---

---

---

---

---

---

... for example:

**NDRL/NIST Solution Kinetics Database on the Web**  
 NIST Standard Reference Database 40  
 A compilation of kinetics data on solution-phase reactions

**Solution Database Search Form**  
 Enter the reactant(s), product(s), and/or solvent(s) in the fields below. Compounds may be entered by formula, name, or CAS number. Multiply-charged species must be entered with the charge specified in the format (+/-)[number]. For example,  $\text{SO}_3^{2-}$  is entered as  $\text{SO}_3-2$ . Fields may be left blank. Press the submit button to start the search. Additional help is available.

**Bibliography Search Form**  
 Fill out one or more of the fields below and press the submit button to start the search.



... results:

**Search Results**

Reference	Reaction	Solvent(s)	Rate constant	Detail
1993MOTSA11842-1845	$\text{MeOH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{OH}$	$\text{H}_2\text{O}$	8.3E8	<a href="#">Detail</a>
1989ELMAC69-74	$\text{MeOH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{OH}$	$\text{H}_2\text{O}$		<a href="#">Detail</a>
1988WUKGRE11-886	$\text{MeOH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{OH}$	$\text{H}_2\text{O}$	9.7E8	<a href="#">Detail</a>
1982WOLWU805-812	$\text{MeOH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{OH}$	$\text{H}_2\text{O}$	1.0E9	<a href="#">Detail</a>
1971WUKGRE11-220	$\text{MeOH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{OH}$	$\text{H}_2\text{O}$	9.7E8	<a href="#">Detail</a>
1969BAXKHA11-24	$\text{MeOH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{OH}$	$\text{H}_2\text{O}$	9.5E8	<a href="#">Detail</a>
1968NETDOR222-230	$\text{MeOH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{OH}$	$\text{H}_2\text{O}$	8.3E8	<a href="#">Detail</a>
1968NETDOR222-230	$\text{MeOH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{OH}$	$\text{H}_2\text{O}$	8.3E8	<a href="#">Detail</a>
1968NETDOR222-230	$\text{MeOH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{OH}$	$\text{H}_2\text{O}$	8.3E8	<a href="#">Detail</a>
1965ADA BOA1417-1424	$\text{MeOH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{OH}$	$\text{H}_2\text{O}$	7.8E8	<a href="#">Detail</a>
1965ADA BOA1417-1424	$\text{MeOH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{OH}$	$\text{H}_2\text{O}$	8.8E8	<a href="#">Detail</a>
1965ADA BOA111-1438	$\text{MeOH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{OH}$	$\text{H}_2\text{O}$	1.2E9	<a href="#">Detail</a>

Search returned 12 records.



**NDRL/NIST Solution Kinetics Database**

**Author(s):** Motohashi, N.; Sato, Y.  
**Title:** Competitive measurement of rate constants for hydroxyl radical reactions using radiolytic hydroxylation of benzoate.  
**Journal:** Chem. Pharm. Bull.  
**Volume:** 41  
**Page(s):** 1842 - 1845  
**Year:** 1993  
**Squb:** 1993MOTSA11842-1845

**Reaction:**  $\text{MeOH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{OH}$   
**Reference reactants:**  $\text{C}_2\text{H}_5\text{CO}_2 + \text{OH}$   
**Solvent(s) and composition(s):**  $\text{H}_2\text{O}$

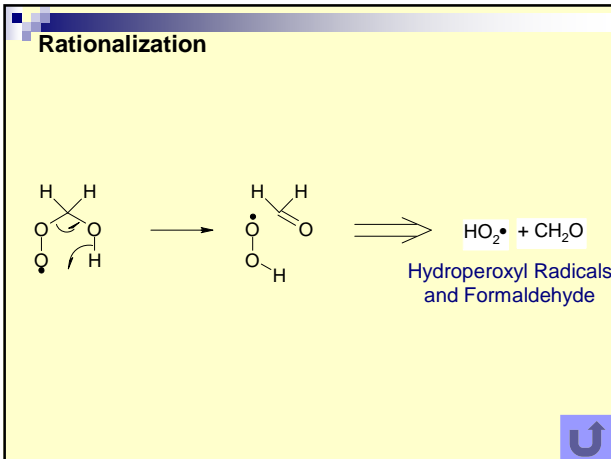
**Reaction data**

Temperature (K)	pH	Pressure (MPa)	Rate constant	Reaction order	Reference rate constant	Quenching rate constant	Ionic strength
75.0			8.3E8	2	8.9E9		

**Data type:** Relative value measured by steady-state method  
**Experimental method:** Gamma radiolysis  
**Analytical technique:** Chromatography  
**Comment:** Competition kinetics

**Reactant details:**  
**Name:** MeOH  
**Formula:**  $\text{C}_2\text{H}_5\text{O}$   
**CAS Number:** 67-56-1  
**Other names:**  $\text{C}_2\text{H}_5\text{OH}$   
**Substance:** Methanol






---

---

---

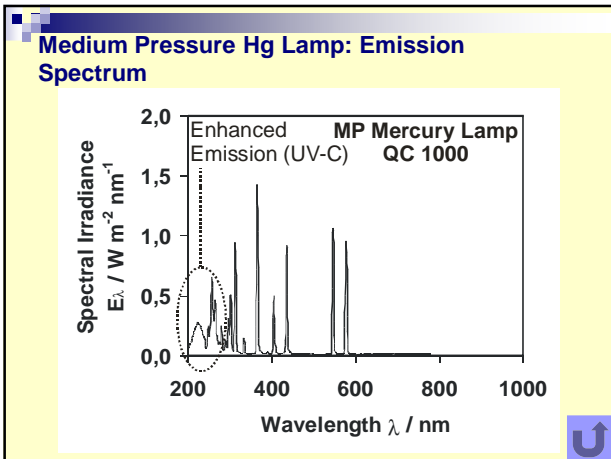
---

---

---

---

---




---

---

---

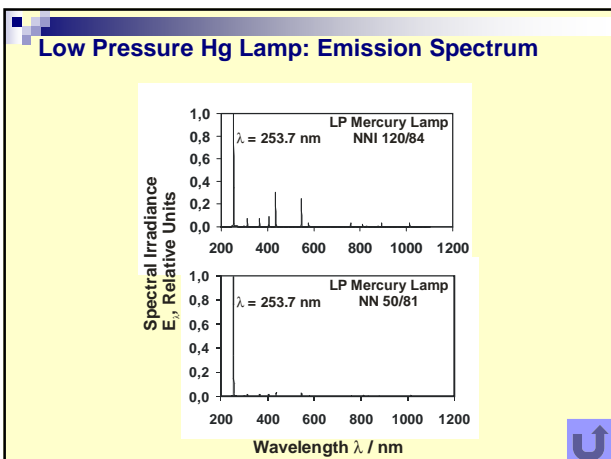
---

---

---

---

---




---

---

---

---

---

---

---

---

Development of Modern Mercury-free Excilamps  
for  
Water and Air Treatment  
and  
Applications in Photochemical Technology  
(Two Lectures)



---

---

---

---

---

---

---

---

### Definition: Elementary Reaction

A reaction for which no *reaction intermediates* have been detected or need to be postulated in order to describe the chemical reaction on a molecular scale.

An elementary reaction is assumed to occur in a single step and to pass through a *single transition state*.

- unimolecular step (or process),
- bimolecular process,
- trimolecular process



---

---

---

---

---

---

---

---