

## Lecture 7. Fundamentals of atmospheric chemistry: Part 2

Objectives:

1. Oxidation-reduction reactions.
2. Reversible reactions. Chemical equilibrium.
3. Lifetime of a species.
4. The steady state principle.
5. Photochemistry: photolysis reactions, photolysis rate coefficient.

Readings: Turco: p. 77 ; Brimblecombe: p. 47-49

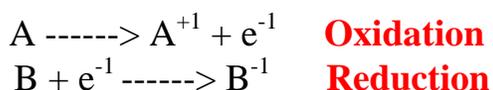
NOTE : In this Lecture we study gas-phase reactions.

Aqueous-phase reactions are discussed in Lecture 13.

### 1. Oxidation-reduction reactions.

Reactions in which one or more electrons are transferred are called oxidation-reduction (or redox) reactions.

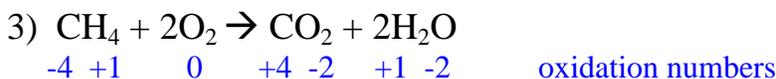
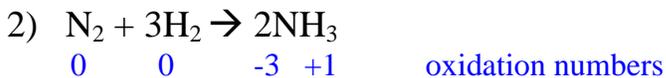
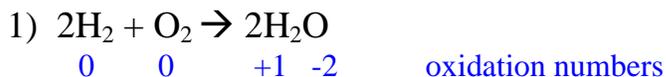
In reaction form these are written:



- These terms are sometimes confusing since the reduction process involves adding an electron. Keep in mind it's the charge that's being reduced in this case. Oxidation receives its name because almost all reactions with oxygen involve some other element losing electrons to the oxygen. Only fluorine would cause oxygen to formally lose electrons. When the term "oxidation" came into use in the early 1800's, fluorine chemistry was unknown, so oxidation was a generally acceptable term.

NOTE: recall Lecture 6, discussion on oxidation number (or state)

Example: some redox reactions



Here carbon changes an oxidation state from -4 in CH<sub>4</sub> to +4 in CO<sub>2</sub>, therefore carbon is oxidized;

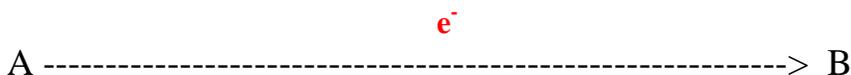
Oxygen changes an oxidation state from 0 in O<sub>2</sub> to -2 in CO<sub>2</sub> and H<sub>2</sub>O, therefore oxygen is reduced;

No change occurs in the oxidation state of hydrogen.

CH<sub>4</sub> is the *reducing agent*, O<sub>2</sub> is the *oxidizing agent*.

NOTE: when the *reducing* or *oxidizing agent is named*, the *whole compound* is specified, not just the element that undergoes the change in oxidation state.

**Summary** of the oxidation-reduction process:



A is a reducing agent  
donates (loses) electrons  
undergoes oxidation  
oxidation number increases

B is an oxidizing agent  
accepts (gains) electrons  
undergoes reduction  
oxidation number decreases

**Electrons lost by A = Electrons gained by B**

NOTE: aqueous-phase redox reactions are discussed in Lecture 13

## 2. Reversible reactions. Chemical equilibrium

For a hypothetical elementary process:



can be written in a form



The type of equilibrium that exist between opposing reactions is called chemical equilibrium. In *chemical equilibrium* the forward and reverse reactions take place with the *same rate*.

Thus, for the reaction above, we have  $\text{Rate}_f = \text{Rate}_r$

Equilibrium constant at a given temperature is equal to the ratio of the equilibrium concentrations of the product to the equilibrium concentrations of the reactants, each raised to their respective coefficients in the balanced chemical equation.

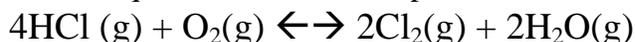
For the reaction above we have:

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b} = \frac{k_f}{k_r}$$

where  $k_f$  and  $k_r$  are the rate constants for forward and reverse reactions, respectively.

- The equilibrium constants have been experimentally determined for many reactions. These constants are available from the tables. Therefore equilibrium constants can be used to find the concentrations of reactants and products for reactions that have reached equilibrium.

**Problem:** Write the equilibrium constant expression for the reaction

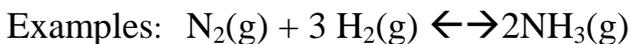


**Solution.**

$$K = \frac{[\text{Cl}_2]^2 [\text{H}_2\text{O}]^2}{\{ [\text{HCl}]^4 [\text{O}_2] \}}$$

**Le Chatelier's principle:** If a stress is applied to a system at equilibrium, the system will adjust to relieve the stress. This principle can be used to predict the effects of changing the concentrations, pressure, or temperature of a reaction at equilibrium.

### **Change of concentration:**



addition of nitrogen or hydrogen at equilibrium will cause a shift to the right and will increase the amount of ammonia.

### **Change of pressure:**

an increase in pressure in reaction above will favor the forward reaction because this reaction reduces the number of molecules and causes a decrease in pressure.

### **Change of temperature:**

an increase in temperature favors the process that absorbs the added thermal heat (endothermic reactions), and a decrease in temperature favors the process that releases the heat (exothermic reactions).

For the reaction above, the forward reaction releases the heat, and the reverse reaction absorbs heat. Therefore, the production of ammonia is favored by lowering T, because this reaction releases heat and counteract the stress of a temperature decrease.

### 3. Lifetime of a species

Consider a hypothetical **first order reaction**



**The half-life,  $\tau$ , of a reaction** is the time required to reduce the concentration of A to half its initial value.

The rate of reaction is (recall Lecture 6)

$$\text{Rate} = - d[A]/dt = k_1 [A]$$

$$d[A]/ [A] = - k_1 dt$$

Integration gives

$$\ln( [A] ) = - k_1 t + \text{const}$$

To define half-life time:  $[A]$  is initial concentration at  $t = 0$

$$[A]/2 \text{ is concentration at } t = \tau$$

$$\text{Then } \tau = \ln(2) / k_1 = 0.693 / k_1$$

- For the first-order reaction the rate constant  $\tau$  is given by the expression

$$\tau = \ln(2) / k_1 = 0.693 / k_1$$

NOTE: that here  $\tau$  does not depend on concentration

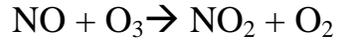
- For the second order reactions  $\tau$  is given by the expression

$$\tau = 1 / (k_2 [A] )$$

- Some second-order reactions can be treated as the pseudo-first order reactions but with appropriate rate constant.

Example: the second-order reaction of ozone with nitric oxide

(see Brimblecombe (1996) p.44-45)



Its rate is

$$\text{rate} = - [\text{NO}] / dt = k_2 [\text{NO}] [\text{O}_3] \quad \text{with } k_2 = 1.8 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1} \text{ at } T = 300\text{K}$$

For typical rural lower atmosphere  $[\text{NO}] \sim 0.5 \text{ ppb}$  and  $[\text{O}_3] \sim 30 \text{ ppb}$

Let's convert units using Loschmidt's number (  $1 \text{ cm}^3$  of air contains  $\sim 2.6 \times 10^{19}$  molec.):

$$\text{Thus } [\text{NO}] = 0.5 \text{ ppb} = 0.5 \cdot 10^{-9} \cdot 2.6 \cdot 10^{19} = 1.3 \cdot 10^{10} \text{ molec. cm}^{-3}$$

$$[\text{O}_3] = 30 \text{ ppb} = 30 \cdot 10^{-9} \cdot 2.6 \cdot 10^{19} = 7.8 \cdot 10^{11} \text{ molec. cm}^{-3}$$

Because  $[\text{O}_3]$  is higher than  $[\text{NO}]$  and  $[\text{NO}]$  will rapidly decline during the reaction, the ozone concentration may be incorporated into the rate constant:

$$- [\text{NO}] / dt = k_2 [\text{NO}] [\text{O}_3] = k_2^* [\text{NO}]$$

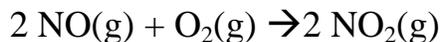
where  $k_2^*$  is a first order constant given by  $k_2 [\text{O}_3]$

- Whenever the concentration of one reactant in a second order reaction is significantly in excess of the other, the reaction can be treated as a first order process with respect to the reactant at low concentration.

#### 4. The steady-state principle.

In chemical kinetics the steady-state approximation is often used for determining the rate of complex, multistep reactions. **Steady-state approximation** assumes that the concentration of **any intermediate** remains constant as the reaction proceeds. An intermediate is neither a reactant nor a product but something that is formed and then consumed as the reaction proceeds.

Example: consider the reaction between nitrogen oxide and oxygen



it may proceed via the following mechanism with two steps:

1.  $\text{NO} + \text{O}_2 \rightleftharpoons \text{NO}_3$  with rate coefficients  $k_1$  and  $k_{-1}$  for forward reaction reverse reactions, respectively
2.  $\text{NO}_3 + \text{NO} \rightarrow 2\text{NO}_2$  with rate coefficient  $k_2$

To apply the steady-state mechanism, we assume that

$$d[\text{NO}_3] / dt = 0$$

i.e., that the concentration of  $\text{NO}_3$  remains constant.

Thus

$$\text{rate of production of } \text{NO}_3 = \text{rate of consumption of } \text{NO}_3$$

In turn,

$$\text{rate of production of } \text{NO}_3 = k_1 [\text{NO}] [\text{O}_2]$$

$$\text{rate of consumption of } \text{NO}_3 = k_{-1} [\text{NO}_3] + k_2 [\text{NO}_3] [\text{NO}]$$

Then

$$k_1 [\text{NO}] [\text{O}_2] = k_{-1} [\text{NO}_3] + k_2 [\text{NO}_3] [\text{NO}]$$

and

$$[\text{NO}_3] = k_1 [\text{NO}] [\text{O}_2] / \{ k_{-1} + k_2 [\text{NO}] \}$$

Let's determine rate of overall reaction of  $\text{NO}_2$  production.

From step 2

$$\text{Rate} = d[\text{NO}_2]/dt = 2 k_2 [\text{NO}] [\text{NO}_3]$$

and

$$\text{Rate} = d[\text{NO}_2] /dt = 2 k_2 [\text{NO}] k_1 [\text{NO}] [\text{O}_2] / \{ k_{-1} + k_2 [\text{NO}] \}$$

Because the stability of  $\text{NO}_3$  is low, we can assume that  $k_{-1} \gg k_2 [\text{NO}]$ , then

$$\text{Rate} = 2 (k_1 k_2 / k_{-1}) [\text{NO}]^2 [\text{O}_2]$$

Thus, overall rate constant is

$$\text{rate constant} = 2 k_1 k_2 / k_{-1}$$

This is entirely consistent with the experimentally observed rate.

- The steady-state approximation is often used when the intermediate species are **free radicals** because they are highly reactive and are consumed at virtually as rapidly as they are formed.

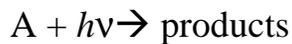
## 5. Photochemistry.

In contrast to redox reactions, the photochemical reactions are initiated by absorption of light.

Photochemistry is the chemistry of atmosphere driven by sunlight.

Photodissociation (or photolysis, or photolytic, or photochemical) reactions

are the cleavage of a molecule into two or more atomic or molecular fragments through the absorption of radiant energy.



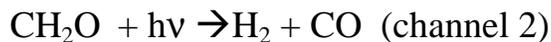
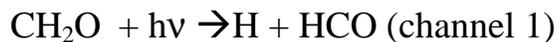
with rate :

$$\text{Rate} = J [A]$$

where **J** is the photolysis rate coefficient for species A. **J** has units  $\text{s}^{-1}$

Example:

1. photolysis of  $\text{NO}_2$  :  $\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$
2. photodissociation of nitric acid:  $\text{HNO}_3 + h\nu \rightarrow \text{OH} + \text{NO}_2$
3. photodissociation of formaldehyde (note: formaldehyde is organic gas):



Photolysis rate coefficient is determined as

$$J = \int \sigma_a(\lambda, T) \Phi(\lambda, T) I_{ac}(\lambda) d\lambda$$

where  $\sigma_a(\lambda, T)$  is the temperature- and wavelength-dependent absorption cross section of a given species (recall Lecture 5),  $\Phi(\lambda, T)$  is the temperature- and wavelength-dependent *quantum yield*, and is  $I_{ac}(\lambda)$  the wavelength-dependent *actinic flux*.

**Quantum yield** is the fraction of the number of photons striking a molecule that results in a dissociation of the molecule to specified products. It gives the efficiency of photolysis.

**Actinic flux** is the radiant flux from all directions on a volume of air. It has units of [photons  $\text{cm}^{-2} \text{s}^{-1} \mu\text{m}^{-1}$ ].

NOTE: typically radiant intensity is in units [ $\text{W m}^{-2} \mu\text{m}^{-1}$ ]. Actinic flux units were converted from [ $\text{W m}^{-2} \mu\text{m}^{-1}$ ] with  $10^{-8} \lambda/hc$ , where  $\lambda$  is assumed to be in  $\mu\text{m}$ ,  $c$  is speed of light in  $\text{cm s}^{-1}$ , and  $h$  is Planck's constant in  $\text{J s}^{-1}$ .

- Most molecules of atmospheric importance photolyze at ultraviolet (UV) wavelengths (such as:  $\text{O}_3$ ,  $\text{O}_2$ , CFCs,  $\text{N}_2\text{O}$ ,  $\text{HNO}_3$ ), but some can be dissociated at visible wavelengths (such as,  $\text{Cl}_2$ ,  $\text{NO}_3$ ,  $\text{NO}_2$ ).

Example: the photolysis rates for photolysis of  $\text{NO}_2$  :  $J_{\text{NO}_2} = 8 \times 10^{-3} \text{ s}^{-1}$  at surface, and  $J_{\text{NO}_2} = 10^{-2} \text{ s}^{-1}$  at 30 km.

NOTE: Photolysis rate for any molecules is determined by a combination of factors: absorption cross section and actinic flux. Actinic flux depends on solar radiation at a given volume of air which depends on season, latitude, altitude, time of the day ( or sun position), atmospheric composition (gases, aerosols, clouds).

Figure 7.1. Absorption cross section for  $O_3$  at 273 K based on data given by DeMore et al (1994).

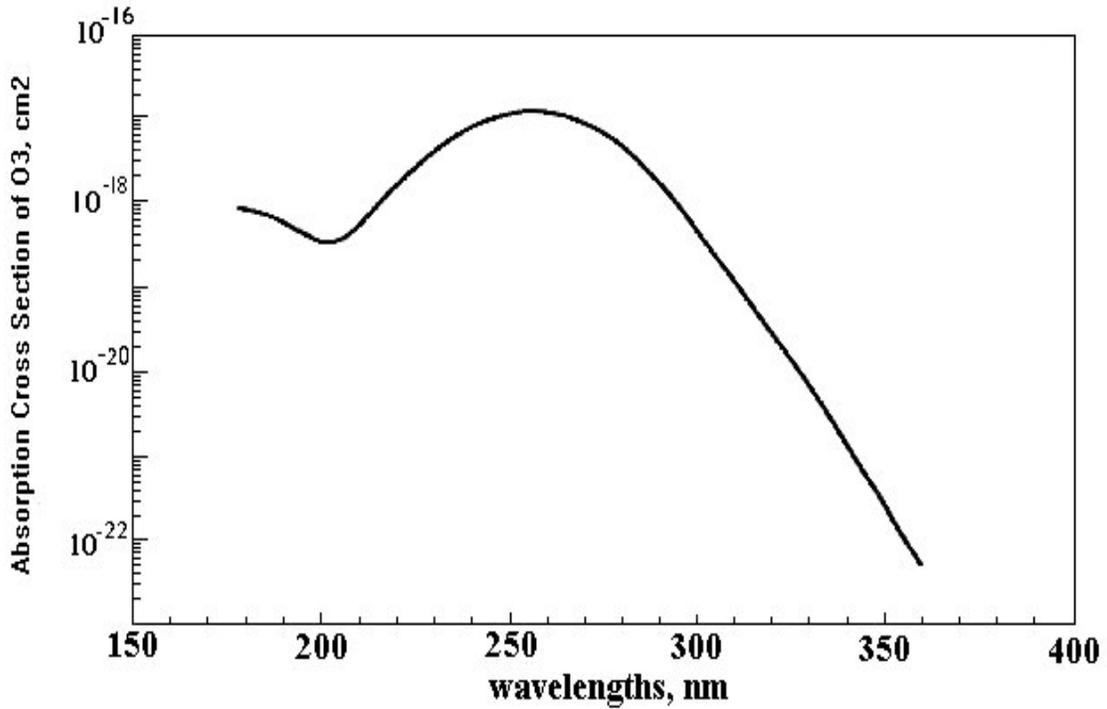
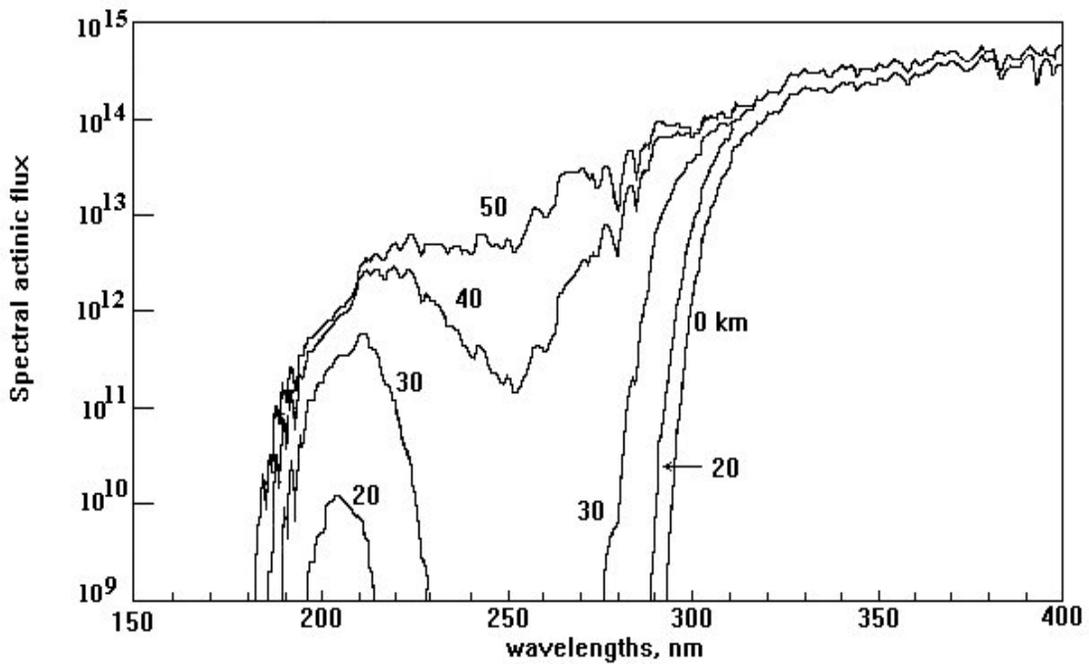
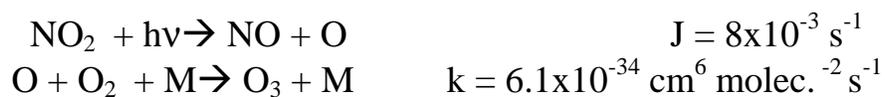


Figure 7.2 Solar spectral actinic flux (photons  $cm^{-2} s^{-1} nm^{-1}$ ) at various altitudes and at the Earth's surface (DeMore et al., 1994).



NOTE: photochemistry is very important in formation of urban pollution (photochemical smog) which will be discussed in Lectures 19-21

**Problem:** The production of ozone in the troposphere begins with photolysis of  $\text{NO}_2$ , by the following mechanism :



Find the rate of ozone production in steady state, if  $\text{NO}_2$  concentration  $[\text{NO}_2] = 2.46 \times 10^{10} \text{ molec.cm}^{-3}$ , and the air density is  $2.46 \times 10^{19} \text{ molec.cm}^{-3}$ .

**Solution.**

Apply steady-state assumption:  $d[\text{O}] / dt = 0$

or: Production rate of  $[\text{O}] =$  Destruction rate of  $[\text{O}]$

Therefore we have:

$$\begin{aligned} J [\text{NO}_2] &= k [\text{O}] [\text{O}_2] [\text{M}] \\ [\text{O}] &= J [\text{NO}_2] / (k [\text{O}_2] [\text{M}]) \end{aligned}$$

Thus

$$\begin{aligned} \text{Rate} &= d[\text{O}_3] / dt = k [\text{O}] [\text{O}_2] [\text{M}] = J [\text{NO}_2] \\ \text{Rate} &= 8 \times 10^{-3} \text{ s}^{-1} \cdot 2.46 \times 10^{10} \text{ molec.cm}^{-3} = 19.68 \times 10^7 \text{ molec.cm}^{-3} \text{ s}^{-1} \end{aligned}$$