Kinetics

Introduction

Chemical Kinetics deals with rate (speed of chemical reactions) - how fast?

Rate equation represents rate, which depends on various reactants

Reaction mechanism is the details of how atoms are rearranged

Reaction Rate

Hypothetical reaction $A_2 (g) + B_2 (g) \rightarrow 2AB (g)$

Show change in concentration in graph below

$H_2 (g) + I_2 (g) \rightarrow 2HI (g)$

Slope of line tangent to curve is a measure of rate
steeper slope is greater rate
positive slope means forming product
negative slope means reactant being used up

(http://www.sparknotes.com/chemistry/kinetics/ratelaws/section1.html)
Consider the reaction $A_2 (g) + B_2 (g) \rightarrow 2AB (g)$

Indicate change with symbols
$\Delta[AB]/\Delta t$ or $d[AB]/dt =$ rate of formation of AB
rate is change in concentration with time

Units for $d[AB]/dt$ are (mol/ L s) or (M/s) or (Ms$^{-1}$)

$-\Delta[A_2]/\Delta t$ or $-d[A_2]/dt =$ rate of loss disappearance of $A_2$

These changes are opposite in sign but not the same in value
for example: 2AB formed for each $A_2$ that disappears so

$$ \frac{1}{2} \frac{d[AB]}{dt} = - \frac{d[A_2]}{dt} $$

Rate of reaction may change with time
so interested in slope and slope at any time

In experiments scientists follow change in concentration by measuring
some property that depends on concentration. Such as: Pressure, acidity,
volume, weight, color, etc…

**Rate Law**

Rate law or rate equation –
mathematical expression relating concentration of
reactants (or products) to reaction rate

Example - for balanced chemical equation

$$ 2N_2O_5 (g) \rightarrow 4NO_2 (g) + O_2 (g) $$
the rate law is
rate = $-d[N_2O_5]/dt = k[N_2O_5]$ 1st order because $[N_2O_5]^1$

where $k$ is called the rate constant and $k$ depends on temperature

****The rate law cannot be determined from a balanced equation.****
It must be determined from experiment ****
To write rate law must express what is changing
\(-d[N_2O_5]/dt\) or \(d[O_2]/dt\) etc.

For balanced chemical equation
\[ \text{NO}_2 (g) + 2\text{HCl} (g) \rightarrow \text{NO} (g) + \text{H}_2\text{O} (g) + \text{Cl}_2 (g) \]

**Experiments show** that Rate = \(k\ [\text{NO}_2][\text{HCl}]\) 2\(^{nd}\) order overall

For
\[ 2\text{NO} (g) + 2\text{H}_2 (g) \rightarrow \text{N}_2 (g) + 2\text{H}_2\text{O} (g) \]

**Experiments show** that
rate = \(k[\text{NO}]^2[\text{H}_2]\) 3\(^{rd}\) order overall

2\(^{nd}\) order in NO 1\(^{st}\) order in \(\text{H}_2\) and 3\(^{rd}\) order overall

Order is the power that concentration is raised to
[ ] means concentration in mol/L

Rate laws can have fractional powers but usually will be integers
Experimental methods to determine rate law

1) Rate Law from Method of Initial Rates
2) Doubling reactant amounts
3) Integrated Rate Law
4) Isolation Method

1. Rate Law from Method of Initial Rates

How to determine rate law experimentally

For \(2\text{NO (g)} + \text{O}_2 \text{(g)} \rightarrow 2\text{NO}_2 \text{(g)}\)
do 5 experiments summarized below:

<table>
<thead>
<tr>
<th>Experiment</th>
<th>\text{NO (mol/L)}</th>
<th>\text{O}_2 \text{(mol/L)}</th>
<th>d[\text{NO}_2]/dt (mmol/Ls) or \Delta[\text{NO}_2]/\Delta t</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>1</td>
<td>7</td>
</tr>
<tr>
<td>B</td>
<td>1</td>
<td>2</td>
<td>14</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>3</td>
<td>21</td>
</tr>
<tr>
<td>D</td>
<td>2</td>
<td>3</td>
<td>84</td>
</tr>
<tr>
<td>E</td>
<td>3</td>
<td>3</td>
<td>189</td>
</tr>
</tbody>
</table>

then assume rate of formation \(d[\text{NO}_2]/dt = k[\text{NO}]^x[\text{O}_2]^y\) and then find \(x, y, \text{ and } k\)

In general \((\text{rate 1/ rate 2}) = (\text{conc 1/ conc2})^x\) where \(x\) is order of reaction with respect to concentration of one reactant.
Must keep all other reactants identical to compare these two experiments.
Example from experiments in chart above

rate\textsubscript{B}/rate\textsubscript{A} becomes
\[
\frac{14}{7} = \frac{k[1]^x [2]^y}{k[1]^x [1]^y}
\]
simplifies to
\[
2 = \frac{[2]^y}{[1]^y}
\]
or
\[
2 = \frac{[2]^y}{[1]^y}
\]
and solving gives
\[
2 = 2^y \quad \text{so} \quad y \text{ must be } y = 1 \quad \text{since} \quad 2^1 = 2
\]

rate\textsubscript{E}/rate\textsubscript{C} becomes
\[
\]
simplifies to
\[
9 = \frac{[3]^y}{[1]^x}
\]
or
\[
9 = \frac{[3]^y}{[1]^x}
\]
and solving gives
\[
9 = 3^x \quad \text{so} \quad x \text{ must be } x = 2 \quad \text{since} \quad 3^2 = 9
\]

And to find \( k \) can pick any reaction and sub in
for example expt D gives
\[
\]
\[
84 = k (4) (3)
\]
\[
84 = 12k
\]
\[
7 = k
\]

And putting it all together the rate law is expressed as

\[
\text{rate} = 7 [\text{NO}]^2 [\text{O}_2]^1
\]
so 2\textsuperscript{nd} order in NO 1\textsuperscript{st} order in \( \text{O}_2 \) 3\textsuperscript{rd} order overall

Does rate law correctly predict rates?
– try expt E put in initial concentrations
\[
\text{rate} = 7[3]^x [3]^y = 7 \cdot 9 \cdot 3 = 189
\]
so predict initial rate is 189 see table – correct!

Rate law can predict rate for any concentrations - tells you how fast
reaction will occur
2. Doubling

Easy way to use is to look at effect of doubling initial concentration while keeping all other concentrations unchanged. If double concentration then rate will either be unchanged, or double, increase by factor of 4 or factor of 8 and order will be 0, 1, 2, or 3, respectively.

<table>
<thead>
<tr>
<th>Order</th>
<th>If Concentration</th>
<th>then and</th>
<th>Rate Increase is</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1 $\rightarrow$ 2</td>
<td>$2^0 = 1$</td>
<td>No change</td>
</tr>
<tr>
<td>1</td>
<td>1 $\rightarrow$ 2</td>
<td>$[A]^1 = 2^1$</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>1 $\rightarrow$ 2</td>
<td>$[A]^2 = 2^2$</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>1 $\rightarrow$ 2</td>
<td>$[A]^3 = 2^3$</td>
<td>8</td>
</tr>
</tbody>
</table>

Example:

if rate of reaction goes eight times faster when concentration of just one reactant doubled what is the order

then $8 = 2^x$ and $8 = 2^3$ so $x = 3$ and so this reactant is 3rd order
3. Integrated Rate Law

How fast does reactant $[A]$ decrease for different order reactions?

**Order: 0**

Rate Law  
Rate $= -d[A]/dt = k$  
Integrated Rate Law  
$[A] = -kt + [A]_0$

![Graph of integrated rate law for order 0](http://www.chem.queensu.ca/people/faculty/mombourquette/FirstYrChem/kinetics/)

**Order: 1**

Rate Law  
$-d[A]/dt = k[A]$  
Integrated Rate Law  
$\ln[A] = -kt + \ln[A]_0$

![Graph of integrated rate law for order 1](http://neon.otago.ac.nz/chemlect/chem201/kinetics/background/background.html)
Order: 2\textsuperscript{nd}

Rate Law \hspace{1cm} Integrated Rate Law
\[ -d[A]/dt = k[A]^2 \Rightarrow \frac{1}{[A]} = kt + \frac{1}{[A]_0} \]

So experiment collect data for the concentration of a reactant versus time
Try plots of \([A]\) \hspace{0.5cm} \ln[A] \hspace{0.5cm} and \hspace{0.5cm} \frac{1}{[A]} \hspace{0.5cm} (y \hspace{0.5cm} axis) \hspace{0.5cm} versus \hspace{0.5cm} time \hspace{0.5cm} (x \hspace{0.5cm} axis)
which either fits straight line best is the order of reaction
if \([A]\) best plot then zero order
if \ln[A] best plot then first order
if \frac{1}{[A]} best plot then second order

Can compare visually or calculate \(r^2\) value which is a measure of quality of fit to straight line where \(r^2 = 1.000\) is a perfect straight line and as \(r^2\) gets smaller then fit is worse so that \(r^2 = 0\) is completely random scatter. Can use software such as EXCEL to plot data, do linear regression, and calculate \(r^2\) values.

Example:
Plots made for \([A]\) vs time \hspace{0.5cm} \ln[A] \hspace{0.5cm} versus \hspace{0.5cm} time \hspace{0.5cm} and \hspace{0.5cm} \frac{1}{[A]} \hspace{0.5cm} versus \hspace{0.5cm} time
and \(r^2\) values \hspace{0.5cm} 0.965 \hspace{0.5cm} for \hspace{0.5cm} [A], \hspace{0.5cm} 0.989 \hspace{0.5cm} for \hspace{0.5cm} \ln[A], \hspace{0.5cm} and \hspace{0.5cm} 0.971 \hspace{0.5cm} for \hspace{0.5cm} \frac{1}{[A]}.

What is the order of the reaction?
Since the \ln[A] versus time gave best fit to a straight line then it must be first order or rate = \(k[A]^1\)
4. Isolation Method (Integrated Rate Law with more than one reactant)

Make reactants much larger in concentration than one of reactants
Focus on low concentration reactant

For example if the balanced equation and rate law are
\[ A + B \rightarrow \text{products} \]
\[ \text{Rate} = k \ [A]^x \ [B]^y \]

To focus on reactant A make it much small
- example set the initial amounts of experiment at

\[ [A]_0 = 0.010 \quad \text{if} \quad [A] \rightarrow 0.000 \quad \text{decrease 100\%} \]
\[ [B]_0 = 1.000 \quad \text{then} \quad [B] \rightarrow 0.990 \quad \text{decrease only 1\%} \]

So \([B]\) is almost constant goes from 1.00 to 0.99 and approximate rate law can be written as

\[ \text{If } k' \text{ is } k' = k[B]_0 \quad \text{then} \quad \text{rate} = k' \ [A]^x \]

If for example \(x = 1\) then Pseudo-first-order rate law
\(x = 2\) then Pseudo-second-order rate law

So if multiple reactants and want to use integrated rate laws to focus on just one reactant
make initial amounts of others in much greater amounts
Example of simple experiment (method of initial rates)

Put one or two identical size pieces of Alka Seltzer tablet in water in plastic film holder and snap on top. Carbon dioxide gas is produced and when enough builds up then the top pops off. The shorter the time to pop the faster the rate of gas production.

![Alka-Seltzer](http://sodiumsymposium.tripod.com/quizzes.html)

Observe results below and then find ratio as shown

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Amount</th>
<th>Time to pop (s)</th>
<th>Rate (1/time) s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1 piece</td>
<td>20</td>
<td>0.050</td>
</tr>
<tr>
<td>B</td>
<td>2 pieces</td>
<td>11</td>
<td>0.095</td>
</tr>
</tbody>
</table>

Ratio of Rates

\[
\text{Rate}_B / \text{Rate}_A = (2/1)^x
\]

\[
.095 / .050 = 1.9
\]

1.9 = 2^x so x = 1 note that there is experimental error so round off

but note that of the choices below only one can fit

2^0 = 1

2^1 = 2 **First Order Reaction**

2^2 = 4

2^3 = 8

*With real experiments data is not perfect*
Temperature Effect on Rates

Increase temperature causes increase in rate for exothermic and endothermic reactions

Rough rule for some reactions is that increase 10°C roughly doubles rate

Area under the curve is the minimum energy required for reaction (Activation energy)

There are more collisions but this is a minor factor (few percent)

Temp Increase (mostly) – more collisions above minimum energy
Rate and Temperature

Observe that increase the temperature then increase the rate
Qualitative: higher temperature the faster the reaction

Graphical Representation

Natural log of $k$ versus Reciprocal Temperature

Quantitative Relationship

$$k = A \, e^{-\frac{E_a}{RT}}$$  \text{Arrhenius Equation}

$k =$ rate constant
$T =$ Temperature
$A =$ frequency factor (same units as first order ($s^{-1}$))
$R =$ gas constant ($8.31 \text{ J/molK}$)
$E_a =$ energy of activation ($J/mol$)
$e = 2.718281\ldots$

Meaning of equation
Contributions due to:

$A$  \text{frequency of collisions and proper orientation}
$e^{-\frac{E_a}{RT}}$  \text{fraction of molecules with sufficient energy}
Activation energy is a multistep process and Ea is the highest barrier.

[Reaction Coordinate Image] (http://www.ucalgary.ca/~kmuldrew/cryo_course/cryo_chap11_1.html)
Catalysts

Catalyst

substance that increase rate of reaction without being used up
changes the mechanism of the reaction and lowers energy of activation.

Lowering Ea speeds up the reaction

Example:

Given T = 400K and
Ea 100kJ/mol \( \Rightarrow \) 50 kJ/mol

\[
\begin{align*}
\text{k (without catalyst)} &= e^{-100000/(8.31)(400)} \sim e^{-30} \\
\text{(k with catalyst)} &= e^{-50000/(8.31)(400)} \sim e^{-15}
\end{align*}
\]

*note units above*

Use \( k = Ae^{-Ea/RT} \) and find

\[
\begin{align*}
k(50kJ) / k(100kJ) &= (Ae^{-15}) / (A e^{-30}) \\
\frac{e^{-15}}{e^{-30}} &= 2.88 \times 10^{-7} / 9.36 \times 10^{-14} \\
&= 10^{-6.5} / 10^{13} \\
&= 10^{6.5} \\
&= 3.16 \times 10^6 \sim 3 \times 10^6 = 3 \text{ million}
\end{align*}
\]

In this example adding catalyst to lower Energy of Activation from 100 to 50 kJ/mol increases rate by a factor of **3 million**!
A catalyst lowers activation energy but the $\Delta H$ remains unchanged.

$\Delta H$ is the difference $E(\text{products}) - E(\text{reactants})$

Two types of Catalysis:

Homogenous in phase with reactants

Heterogeneous in different phase than reactants
Energy of Activation ($E_a$)

Energy changes associated with reaction described in transition state theory

$$A_2 + B_2 \rightleftharpoons \frac{A}{| |} \rightarrow A-B \text{ and } A-B$$

Activated Complex: Unstable arrangement that exists only for a moment
Also called Transition State

Can either go back to reactants or go on to the products

---

On the left is a potential energy diagram for the changes occurring in a chemical system during an exothermic reaction. On the right is the same type of diagram for an endothermic reaction.

(http://www.ucdsh.on.ca/tiss/stretton/chem2/rate03.htm)

Energy of Activation ($E_a$) is the potential energy barrier
The lower the $E_a$, the faster the reaction
The higher the temperature ($T$), the faster the reaction

so to make reaction go faster can add catalyst or raise temperature
Kinetics

Rate Equations of Single Step Reactions

Molecularity: number of molecules that participate in individual reactions

Unimolecular Step  If only one step in reaction
A \rightarrow \text{ products} \quad \text{Rate} = k[A]

Bimolecular Step
A + A \rightarrow \text{ products} \quad \text{Rate} = k[A]^2
A + B \rightarrow \text{ products} \quad \text{Rate} = k[A][B]

Termolecular Step (unusual for 3 body collisions to occur)
A + A + A \rightarrow \text{ products} \quad \text{Rate} = k[A]^3
A + A + B \rightarrow \text{ products} \quad \text{Rate} = k[A]^2[B]
A + B + C \rightarrow \text{ products} \quad \text{Rate} = k[A][B][C]

In multistep reaction must combine various individual steps
Such a combination of steps is called the mechanism of a reaction

**Can write rate law for a step of a mechanism but not balanced equation**

Single Step Reactions

Some reactions occur in single step

\[ \text{CO (g)} + \text{NO}_2 (g) \rightarrow \text{CO}_2 + \text{NO (g)} \]

\[ \text{CO (g)} + \text{NO}_2 (g) \rightarrow \text{O}—\text{N}—\text{O}—\text{C=O} \rightarrow \text{N=O} + \text{O=C=O} \]

Understand single step reaction

\[ \text{A}---\text{A} \leftrightarrow \text{A}–\text{B} \quad \text{and} \quad \text{A}–\text{B} \leftrightarrow \text{B}---\text{B} \]

Bonds break and form simultaneously

But not all collisions are effective
Factors that affect collision effectiveness—
  Orientation: Proper position (steric hindrance and factors)
  Frequency: Number of collisions
  Energy: Minimum energy
Reaction Mechanism

Mechanism is the detailed steps involved in reaction

Ex:
\[
\text{NO + F}_2 \rightarrow \text{ONF} + \text{F} \quad \text{Step 1}
\]
\[
\text{NO} + \text{F} \rightarrow \text{ONF} \quad \text{Step 2}
\]
\[
2\text{NO} (\text{g}) + \text{F}_2 (\text{g}) \rightarrow 2\text{ONF} (\text{g}) \quad \text{Overall Reaction}
\]

F is the reaction intermediate which is a substance produced and used up in reaction but not a reactant or product

Detailed molecular steps that carry a reaction from reactants to products

Example:
\[
2\text{NO} + \text{F}_2 \rightarrow 2\text{ONF} \quad \text{(nitrosoyl fluoride)}
\]

observed experimental rate = k[NO][F$_2$]

Mechanism to explain rate

Slow: 1) NO + F$_2$ → ONF + F \hspace{1cm} k$_1$[NO][F$_2$]

Fast: 2) F + NO → ONF \hspace{1cm} k$_2$[F][NO]

\[
2\text{NO} + \text{F}_2 \rightarrow 2\text{ONF}
\]

Note:
\text{Can} write rate law if given a step of mechanism
\text{Cannot} write rate law for balanced chemical equation

Two bimolecular steps but F reaction intermediate and is used up rapidly so

Step 1 is the slow step
Step 2 is the fast step

Rate = rate 1 + rate 2 \hspace{1cm} \text{and if rate = slow + fast then rate = slow step}

(http://mooni.fccj.org/~ethall/2046/ch12/rdetstep.htm)
Example:
If Step below is the rate determining step of mechanism
Hydroxide Methyl bromide Methanol Bromide
OH\(^{-}\) + CH\(_3\)Br \(\rightarrow\) CH\(_3\)OH + Br\(^{-}\)

then \(\text{Rate} = k[\text{OH}^{-}][\text{CH}_3\text{Br}]\)

OH\(^{-}\) + CH\(_3\)Br \(\rightarrow\) HO\(^{-}\)--CH\(_3\)--Br \(\rightarrow\) H—O—CH\(_3\) + Br\(^{-}\)

Reactants Transition State Products

If given balanced chemical equation then **cannot** tell the mechanism
If given mechanism **can** add steps to get balanced chemical equation.

Can guess at mechanism or do more experiments to determine
First Order and Half-life

Half-life normally used for first order - *all radioactive decay is first order*

For every half life ($t_{1/2}$) of time that passes, half of concentration disappears

$$k \ t_{1/2} = \ln(2)$$ or rearranged to $$t_{1/2} = \frac{\ln(2)}{k}$$

$t_{1/2} = $ half life
$k = $ rate constant

Note - can derive equation from first order kinetics

$$\ln[A] = -k \ t + \ln[A_0]$$
$$\ln[A] = -k \ t_{1/2} + \ln[A_0]$$
$$k \ t_{1/2} = \ln[A_0] - \ln[A]$$
$$k \ t_{1/2} = \ln([A_0]/[A])$$ and if $([A_0]/[A]) = 2$ then

$$k \ t_{1/2} = \ln(2)$$

**Example:**
If half life is 20 seconds $t_{1/2} = 20$ s then what is rate constant?

$$k \ t_{1/2} = \ln(2)$$

$(k) (20 \text{ sec}) = \ln(2)$

$k = 0.0347 \text{ s}^{-1}$
and note that units work out
-\( \frac{d[A]}{dt} = k \cdot [A] \)
(mol/L s) = (1/s) (mol/L) units

More in notes on radioactivity but if know [A], k, and [A_0]
then use \( \ln[A] = -k \cdot t + \ln[A_0] \) to find time \( t \) that has passed

on exam will give:
\( k \cdot \frac{t}{2} = \ln(2) \) or \( k \cdot \frac{t}{2} = .693 \)
and \( \ln[A] = -k \cdot t + \ln[A_0] \)

Example of Enzyme Kinetics

\( 2\text{H}_2\text{O}_2 \text{(aq)} \) (with catalase \( \text{(aq)} \)) \( \rightarrow \) \( \text{O}_2 \text{(g)} + 2\text{H}_2\text{O} \text{(l)} \)

1 molecule of the enzyme catalase (also called peroxidase)
can cause 5 million \( \text{H}_2\text{O}_2 \) molecules to break apart every second!

\( \text{H}_2\text{O}_2 \) is formed as a byproduct in cells but is a poison and must be removed or it would oxidize and break apart other molecules in cell.

Enzymes act as catalysts living systems
enzymes are complex proteins
(proteins made of amino acids)

Thousands of enzymes in cells enable specific reactions to be carried out millions of times faster than they would without enzyme (biological catalyst)
Example Kinetics in the Environment (a chain mechanism)

Ozone (O$_3$) Layer in upper atmosphere protects us from too much ultraviolet (UV) light

Freon-12 and other molecules if released into atmosphere eventually break apart due to exposure to UV light high in atmosphere

$$CCl_2F_2 (g) + UV \text{ light } \rightarrow CClF_2 (g) + Cl\cdot (g)$$

Cl• (g) is a free radical unpaired electron and very reactive

Mecahanism

<table>
<thead>
<tr>
<th>Cl•</th>
<th>+</th>
<th>O$_3$</th>
<th>→</th>
<th>ClO•</th>
<th>+</th>
<th>O$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O•</td>
<td>+</td>
<td>ClO•</td>
<td>→</td>
<td>Cl•</td>
<td>+</td>
<td>O$_2$</td>
</tr>
</tbody>
</table>

so overall

O• + O$_3$ → 2O$_2$

ozone destroyed

One Cl• repeats cycle above over and over and destroys thousands of ozone molecules!

So the Equilibrium in upper atmosphere is shifted and O$_3$ destroyed

O• + O$_2$ (mostly) ⇌ O$_3$ (small amount)

Excess ultraviolet light can cause:

- Skin cancer
- Crop damage
- Cataract (clouding of lens of eye)

Further Information - From Introduction to Ozone website

“Ozone in the Stratosphere

Ozone and oxygen molecules in the stratosphere absorb ultraviolet light from the sun, providing a shield that prevents this radiation from passing to the earth's surface. While both oxygen and ozone together absorb 95 to 99.9% of the sun's ultraviolet radiation, only ozone effectively absorbs the most energetic ultraviolet light, known as UV-C and UV-B, which causes biological damage. The protective role of the ozone layer in the upper
atmosphere is so vital that scientists believe life on land probably would not have evolved - and could not exist today - without it.

The term "shield" as a description of ozone in the stratosphere is a bit misleading because the molecules do not form an impermeable sphere around the earth. Ozone continuously breaks apart into its oxygen atoms and reforms as ozone molecules, so a particular ozone molecule doesn't last very long. The "shield" changes constantly, but the atmospheric chemical processes maintain a dynamic equilibrium that keeps the overall amount of ozone constant - that is, it would if humans did not contribute to the chemical processes.

About 90% of the ozone in the earth's atmosphere lies in the region called the stratosphere between 16 and 48 kilometers (10 and 30 miles) above the earth's surface. Ozone forms a kind of layer in the stratosphere, where it is more concentrated than anywhere else, but even there it is relatively scarce. Its concentrations in the ozone layer are typically only 1 to 10 parts of ozone per 1 million parts of air, compared with about 210,000 parts of oxygen per 1 million parts of air."