

Air Pollution and Environmental Chemistry

The facts:

Man-made emissions have contributed to two conditions that are under close scrutiny by the scientific community and the developed nations world-wide.

1. Global warming which is an increase in Green House Gases
2. Ozone depletion in upper stratosphere

Q.

What is the public's perception of the facts?

A.

Depends on which side of the political arena you are on. Until very recently, partisan politicians have denied and distorted the facts to John Q. Public.

Respect for science and its findings has been diminished due to wishful thinking...

We all like to “hide our heads in the sand” sometimes, but at what cost?

The **Greenhouse Effect** is the process in which the emission of infrared radiation by the atmosphere warms a planet's surface. The name comes from an incorrect analogy with the warming of air inside a greenhouse compared to the air outside the greenhouse. The greenhouse effect was discovered by Joseph Fourier in 1824 and first investigated quantitatively by Svante Arrhenius in 1896. The Earth's average surface temperature of 14 °C (57 °F) would otherwise be about -19 °C (-2.2 °F) in the absence of the greenhouse effect. Global warming, a recent warming of the Earth's lower atmosphere, is believed to be the result of an enhanced greenhouse effect due to increased concentrations of greenhouse gases in the atmosphere. In addition to the Earth, Mars and Venus have greenhouse effects.

The Earth receives energy from the Sun in the form of radiation. Most of the energy is in visible wavelengths and in infrared wavelengths that are near the visible range (often called "near infrared"). The Earth reflects about 30% of the incoming solar radiation. The remaining 70% is absorbed, warming the land, atmosphere and oceans.

For the Earth's temperature to be in steady state so that the Earth does not rapidly heat or cool, this absorbed solar radiation must be very closely balanced by energy radiated back to space in the infrared wavelengths. Since the intensity of infrared radiation increases with increasing temperature, one can think of the Earth's temperature as being determined by the infrared flux needed to balance the absorbed solar flux. The visible solar radiation mostly heats the surface, not the atmosphere, whereas most of the

infrared radiation escaping to space is emitted from the upper atmosphere, not the surface. The infrared photons emitted by the surface are mostly absorbed in the atmosphere by greenhouse gases and clouds and do not escape directly to space.

The molecules/atoms that constitute the bulk of the atmosphere: **oxygen** (O_2), **nitrogen** (N_2) and **argon** (Ar); do not interact with infrared radiation significantly. While the oxygen and nitrogen molecules can vibrate, because of their symmetry these vibrations do not create any transient charge separation. Without such a transient **dipole** moment, they can neither absorb nor emit infrared radiation. In the Earth's atmosphere, the dominant infrared absorbing gases are **water vapor**, **carbon dioxide**, and **ozone** (O_3). The same molecules are also the dominant infrared emitting molecules. CO_2 and O_3 have "floppy" vibration motions whose quantum states can be excited by collisions at energies encountered in the atmosphere. For example, carbon dioxide is a linear molecule, but it has an important vibrational mode in which the molecule bends with the carbon in the middle moving one way and the oxygens on the ends moving the other way, creating some charge separation, a **dipole moment**, thus carbon dioxide molecules can absorb IR radiation. Collisions will immediately transfer this energy to heating the surrounding gas. On the other hand, other CO_2 molecules will be vibrationally excited by collisions. Roughly 5% of CO_2 molecules are vibrationally excited at room temperature and it is this 5% that radiates. A substantial part of the greenhouse effect due to carbon dioxide exists because this vibration is easily excited by infrared radiation. (Wikipedia)

Panels/Groups convened over the last decades to discuss environmental concerns

(1) IPCC Intergovernmental Panel on Climate change
 “The Panel was established in 1988 through a resolution of the UN General Assembly. One of its clauses was significant in having stated, “Noting with concern that the emerging evidence indicates that continued growth in atmospheric concentrations of “greenhouse” gases could produce global warming with an eventual rise in sea levels, the effects of which could be disastrous for mankind if timely steps are not taken at all levels. This means that almost two decades ago the UN was acutely conscious of the possibility of disaster consequent on climate change through increases in sea levels. Today we know much more, which provides greater substance to that concern.”

Speech by R K Pachauri, Chairman, IPCC

Oslo, 10 December 2007 in Acceptance of the Nobel Peace Prize shared with Al Gore. Nobel citation: “for their efforts to build up and disseminate greater knowledge about man-made climate change, and to lay the foundations for the measures that are needed to counteract such change”.

IPCC is the Panel (established in 1988 through a resolution of the UN General Assembly) that first convened scientists from several industrialized nations in the early 1990's. The conclusion was that the planet's temperature would increase by $1.7 - 3.8^{\circ}\text{C}$ by 2100. The ultimate prediction is that the sea level would rise between 15 and 90cm.

DISASTER!!

Up until the last IPCC report (Fourth Report) in 2007, many politicians (and scientists) doubted the scientific basis of global warming due to CO_2 emissions. The new report put an end to all discussion. Prepared by scientists all over the world, it placed the reality of human-induced climate change beyond any doubt.

(2) Montreal Protocol

The **Montreal Protocol on Substances that Deplete the Ozone Layer** is an international treaty designed to protect the ozone layer by phasing out the production of a number of substances believed to be responsible for ozone depletion. The treaty was opened for signature on September 16, 1987 and entered into force on January 1, 1989 followed by a first meeting in Helsinki, May 1989. Since then, it has undergone seven revisions, in 1990 (London), 1991 (Nairobi), 1992 (Copenhagen), 1993 (Bangkok), 1995 (Vienna), 1997 (Montreal), and 1999 (Beijing). Due to its widespread adoption and implementation it has been hailed as an example of exceptional international cooperation with Kofi Annan quoted as saying it is "Perhaps the single most successful international agreement to date...".^[1] (Wikipedia)

Kofi Atta Annan is a Ghanaian diplomat who served as the seventh Secretary-General of the United Nations from January 1, 1997 to January 1, 2007, serving two five-year terms. Annan was the co-recipient of the Nobel Peace Prize in 2001.

(3) **Kyoto Climate Protocol**

The **Kyoto Protocol** is a [protocol](#) to the international [Framework Convention on Climate Change](#) with the objective of reducing [Greenhouse gases](#) that cause [climate change](#).

It was agreed on [11 December 1997](#) at the [3rd Conference of the Parties](#) to the treaty when they met in [Kyoto](#), and entered into force on [16 February 2005](#) following ratification by Russia. As of November 2007, [175 parties](#) have ratified the protocol. Of these, 36 developed countries (plus the [EU](#) as a party in its own right) are required to reduce greenhouse gas emissions to the levels specified for each of them in the treaty (representing over 61.6% of emissions from Annex I countries), ^{[1][2]} with three more countries intending to participate.^[3] One hundred and thirty-seven (137) developing countries have ratified the protocol, including [Brazil](#), [China](#) and [India](#), but have no obligation beyond monitoring and reporting emissions. The [United States](#) has not ratified the treaty. Among various experts, scientists and critics there is some debate about the usefulness of the protocol, and there have been [cost-benefit](#) studies performed on its usefulness. (Wikioedia)

Target dates of Kyoto Protocol are:

The requirement is to comply from 2008-2012

The goal is to lower overall emissions of six greenhouse gases – carbon dioxide, methane, nitrous oxide, sulfur hexafluoride, hydrofluorocarbons and perfluorocarbons

Mandate of Kyoto Treaty is that industrialized countries must reduce their collective emissions of greenhouse gases in the 2008-2012 period by 5.2% compared to the year 1990 levels. Bottom line: (Note that as compared to the expected emission by 2010 without the Protocol, this limitation represents about a 29% cut). The national limitations range from 8% in the European Union, 7% for the US, 6% for Japan, 0% for Russia, and permits increases of 8% for Australia and 10% for Iceland.

Problem is, many in the US think that is is placing unrealistic demands on us to cut our emissions, such that we will not ratify the treaty.

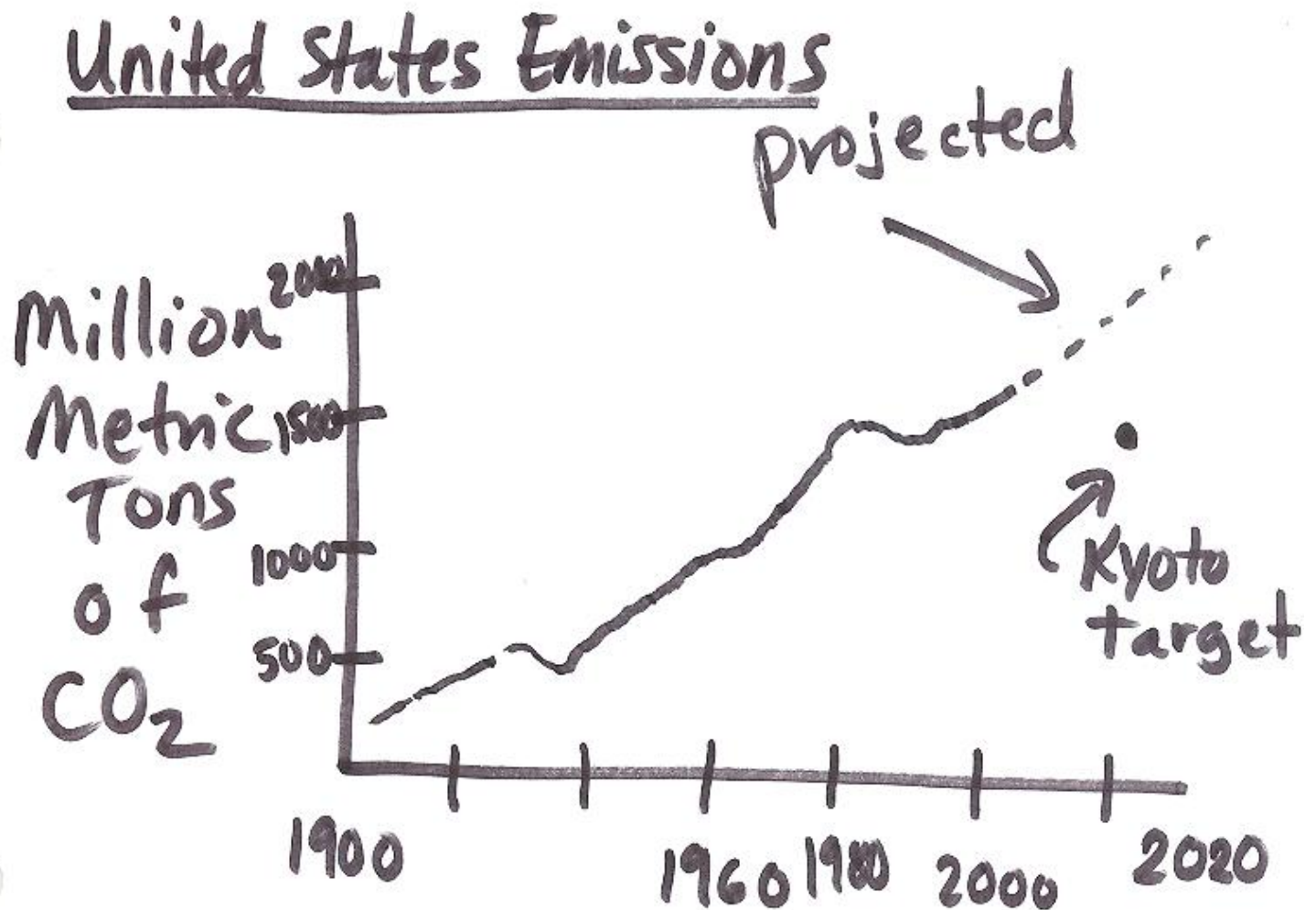
Q.

What can we do?

A.

Emissions trading among nations. In other words, an industrialized nation that doesn't want to reduce its emissions could "buy" a permit from another industrialized nation that would reduce its own emissions less to account for the required decrease of emissions.

United States Emissions



Kyoto target is not thought to be feasible for the U.S.

Grave economic consequences would ensure if we had to cut back so much on fossil fuel burning.

Q.

What about alternative, cleaner fuels?

A.

Until very recently, the U.S. has invested very little money in research based on solar conversion, alternative fuel vehicles (main reason is that industry has no incentive to “waste” money on such research – it is more expensive technology than fossil fuel burning technology). The attitude has changed recently, however, as industry has been made to believe that there is money to be made from green, “earth-friendly” alternatives. hybrid cars etc.,

Clearly, the Kyoto Climate Treaty and resulting Protocol is a good place to start, and, with time, it will allow for implementation of goals. Time is running out, though, if you listen to scientific forecasts.

Houston Air

- Houston Ship Channel in Texas
 - >100 large industrial manufacturing and chemical plants / oil refineries

- Largest concentration of petrochemical companies in the United States
- Population of Houston is > 4 million people so car emissions are also enormous

Houston pollution is said to exceed the Los Angeles metropolitan area.

Houston Air – Quality Study

\$20 million dollars was spent in Aug – Sept 2000 to gather data on air quality in Houston

- 300 researchers and over 40 public and private institutions were involved in the project
- Six aircraft made daily sampling flights
1,500 – 2,500 feet mid-level
300 – 40,000 feet two extremes
to study vertical distribution of pollutants and ozone precursor compounds
- Approx. 20 ground-based air quality stations in eastern Texas measured chemicals with much more sophisticated equipment than what is normally used.

100 organic compounds were detected

25 were monitored on a continuous basis including:

O_3 , SO_2 , NO_2 , NO

Biggest concern is O_3 in lower atmosphere for health of Houston occupants. O_3 plume extends hundreds of miles from Houston deep into Texas.

Clean air in Texas:

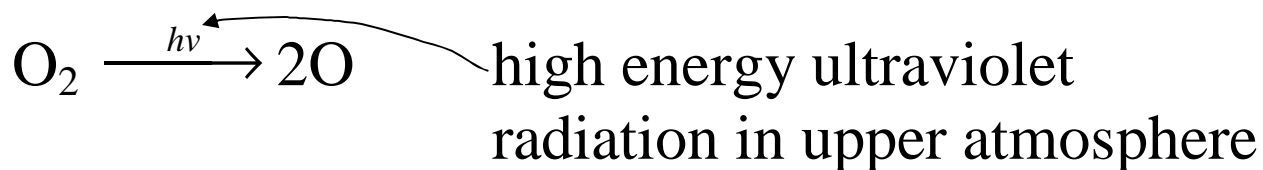
40 ppb	O_3	clean air
>80 ppb	O_3	stagnant air sometimes reaches this level but often exceeds 80
120 ppb	O_3	is considered to be limit of “safe air”

Supreme Court wants to toughen standards to be less than 120 ppb

Houston is sometimes 250 ppb which is way above the level to damage lungs

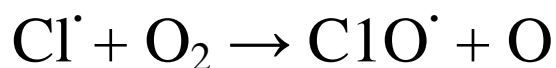
Q. Where is O_3 coming from?

A. Normally it come from O atoms



In lower atmosphere, free radicals such as Cl^\cdot coming from $\text{Cl}_2 \xrightarrow{h\nu} 2\text{Cl}^\cdot$

(Houston uses a lot of Cl_2 in the chemical industry)



Also, car exhaust forms free radicals and O atoms result.

Haze Particles

Blankets of tiny aerosol droplets coming from SO_2 that turns into H_2SO_4 droplets. This haze in the upper atmosphere helps to offset global warming problems due to its ability to reflect back more of the sun's radiation to outer space before it reaches the earth.

So one pollution problem actually helps alleviate another pollution problem in this case!

Environmental Chemistry – An overview

A better understanding of environmental chemistry can be obtained if it is viewed in perspective of global energy needs and use, the consequences of such use and the disposal of wastes and other products.

In this topic we present an overview of the subject, as it pertains to this course, and consider the following factors:

Energy uses

Disposal of chemicals and wastes

Toxicity of chemicals and wastes

Pollution of water, air and soil

Energy Needs – Use of Fuels

Our energy needs are presently being met by the combustion of carbon-containing compounds and, to a lesser extent, by nuclear fuels. The pollution problems that result from such use are presented below. The fossil fuels of concern to us are methane (CH_4), gas, oil, and coal.

I. The Greenhouse Effect

A. Natural Greenhouse Effect and Gases

The **greenhouse effect** is the term given to the *natural insulating effect* of the earth's atmosphere due primarily to the presence of **greenhouse gases** that occur naturally. Natural greenhouse gases are CO_2 , CH_4 and N_2O (nitrous oxide). Their presence is necessary, as they help maintain the earth's energy balance and keep it from cooling down. Energy from the sun is prevented from reaching the earth by many processes including reflection from clouds and absorption by clouds. In addition, the surface of the earth, as it cools, radiates a great deal of the energy it has absorbed back up into the atmosphere (called **reradiation**).

Fortunately, some of this **reradiation** is absorbed by the carbon dioxide and water in the upper atmosphere and subsequently radiated back to the surface of the earth. In this way, additional heat is kept within the lower atmosphere. **This warming by absorption and reemission of radiation is a more technical definition of the greenhouse effect.**

B. Unnatural Sources of Greenhouse Gases – Global Warming

As you know there is considerable concern about enhancement of greenhouse effect. This concern stems from the fact that there has been a huge increase in the greenhouse gases from unnatural sources, mainly the burning of fossil fuels. The atmosphere receives CO_2 from many sources including respiration of plants and animals, forest fires and the burning of vegetable matter. This CO_2 production is in delicate balance with the uptake of CO_2 by plants for photosynthesis and by the oceans that absorb CO_2 and precipitate it as MgCO_3 and CaCO_3 . After these natural uses of CO_2 , there is only 5% left over. Most of this 5% comes from the burning of coal and oil. If we continue to add more CO_2 at the present rate, it is thought by some that the surface of the earth may be warmed by several degrees in the next 15 years. Even such a slight warming would cause the polar ice caps to melt and would cause other climatic changes.

Current Status of global warming in 2008

The issue of global warming by the excess CO_2 in the atmosphere is no longer the hotly debated topic that it was even several years ago. One alarming conclusion came early on by the IPCC in 1992 that we would be experiencing even more pronounced effects of global warming if not for some cancellation of the accelerated greenhouse effect by **haze particles** in the upper atmosphere. Haze particles are large blankets of tiny aerosol droplets that originate from volcanic eruptions or from fuel burning that produces SO_2 that turns into sulfuric acid droplets. This haze serves to reflect more of the sun's radiation back to space before it even reaches the earth. The haze is not expected to be able to compensate for the greenhouse effect over a period of several decades, however.

Thus, according to these estimates, the continuing combustion of fossil fuels may result in our reaching the upper limit of CO_2 tolerance soon, and for this reason some researchers suggest that alternate fuels, such as nuclear, be used. Clearly, the greenhouse effect is a serious problem worthy of constant monitoring.

II. Sulfur dioxide emissions

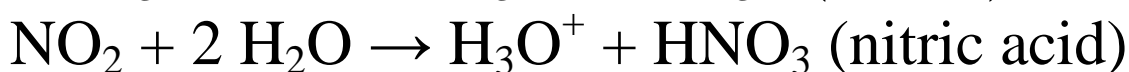
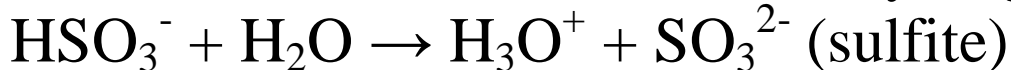
Oil and coal contain large amounts of sulfur. Combustion of these fuels results in the emission of sulfur dioxide into the atmosphere. The sulfur content of an oil depends on its source. There are very few oils that do not contain sulfur. Oil obtained from the North Sea contains 1% S by weight. Oils from the Middle East contain 4-5% sulfur. All sulfur in crude oil is present as organic molecules, mostly thiophene, C_4H_4S . Coal can contain several percent by sulfur weight, depending on its source. The sulfur in the coal is present both as organic sulfur and also in the form of metal sulfides, such as FeS_2 . The sulfur in the oil processed by an average refinery (100,000 barrels per day) amounts to 713 million lbs. of SO_2 per year.

It should be realized that 80% of the SO_2 put into the atmosphere in the United States comes from fuel combustion (power plants) and it amounts to 26.5 million tons of SO_2 per year released into the atmosphere. Furthermore, shale oil, a potential fuel for future use, contains 2% N by weight which must be removed prior to burning the fuel or otherwise nitrogen

oxides, which are both toxic and also produce acid rain, would be released in the atmosphere.

III. Acid Rain

Acid Rain results from the reactions of SO_x ($\text{SO}_2 + \text{SO}_3$) and NO_x ($\text{NO} + \text{NO}_2$) with water. Examples of such acids are below:



(HSO_3^- and SO_3^{2-} are related to H_2SO_3 which is sulfurous acid)

The acids thus produced are carried down from the atmosphere to the soil during precipitation. It is important to remember that acid rain will fall on areas that are far removed from the location of the pollution. This occurs because SO_x and NO_x form stable aerosols in the atmosphere and thus move over the globe. An aerosol is a relatively stable colloidal suspension of gases, liquid and solids in air. When these settle, acid rain is produced. Many lakes in the world are now polluted because of acid rain. At a pH of 4.0 damage to

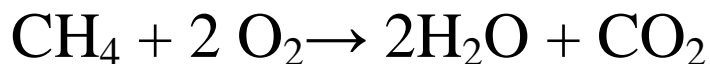
aquatic life occurs. The presence of CO_2 in water cannot account for this acidity, as a pH 5.5 results upon CO_2 saturation of a clean lake. Beginning in the early 1970's, numerous lakes in the world have become too acidic to support aquatic life.

The pollution of lakes, because of acid rain, appears now to be more complicated than originally thought. Some lakes have a pH of 4 but the aquatic life survives, whereas in others it fails. This has now been attributed to the presence of aluminum in the water which results upon acidification of a lake. Aluminum collects in the gills of fish and prevents them from breathing, thus suffocation occurs. If the sediment of a lake is not rich in aluminum-containing minerals, apparently no harm is done.

IV. Combustion of Fossil Fuels

1. Methane

The combustion (total oxidation) given by the equation



Is exothermic, $\Delta H = -192$ kcal/mole, or 192 kcal of heat **released** per 16g of fuel. Methane, found naturally, is considered to be a clean fuel, its use contributing primarily CO_2 to the atmosphere.

2. Coal

Coal is primarily a mixture of complex organic compounds and consists by weight typically of 65% C, 5% H, 1% O and 10-12% water as moisture. Organic and inorganic compounds containing sulfur are also present. Furthermore, coal also contains hydrocarbon compounds with nitrogen atoms. All of these will produce both SO_2 and NO_2 upon combustion of the coal. Thus, pollution prevention in this case could be accomplished if SO_2 , SO_3 and NO_x were “scrubbed off” instead of released in the atmosphere. It would be clearly uneconomical to remove S and N-containing materials from coal prior to its combustion.

3. Oil

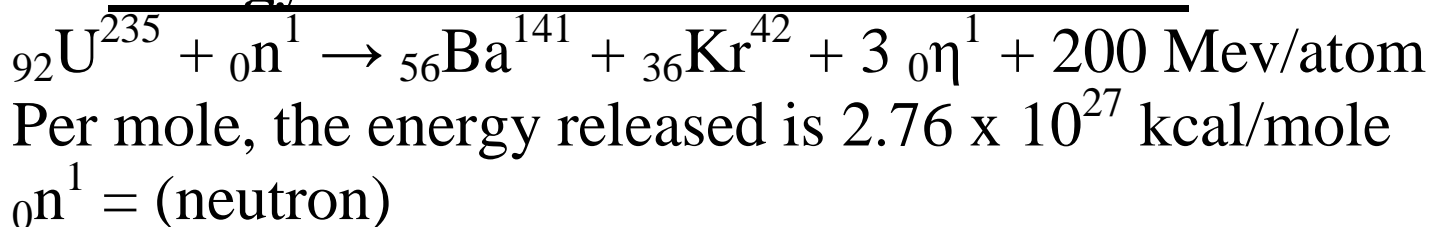
Oil combustion will also result in the formation of oxides of sulfur and nitrogen. Their removal for environmental reasons must also be achieved to prevent SO_2 and NO_2 emissions.

V. Nuclear Fuels and Radioactive Compounds

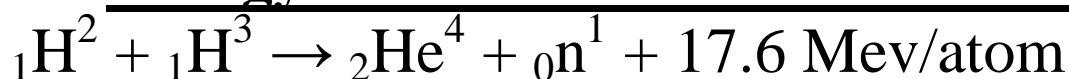
A. Nuclear Fuels

Although nuclear fuels can be considered “clean” they can cause even more serious problems than fossil fuels, as they can release radioactive materials into the environment; for this reason they are accepted only reluctantly. However, the oil and coal supplies of the world will dwindle with use and people will have to depend on alternate fuel sources. Now let us compare the energy release from heating gas or coal with that released by nuclear fuels on a per mole or weight basis.

a. **Energy released from Fission Reactions**



b. **Energy released from Fusion Reactions**



${}_1\text{H}^2$ is deuterium (D); ${}_1\text{H}^3$ is tritium (T)

Per mole, the energy released is 2.3×10^{32} kcal/mole

Clearly, nuclear reactions are unlike chemical reactions. The aforementioned fission reaction served as the basis for the first atomic bomb exploded in 1945.

In comparison, one mole of methane releases only 192 kcal/mole, thus the fusion reaction on a per mole basis releases 10^{30} times more energy. The advantage of the nuclear fuels is thus very obvious.

The problem presented by the nuclear fuels are:

- leakage of radioactive species from nuclear reactors
- potential for malignancies due to such radioactivity
- difficulty in disposing of nuclear wastes

B. Radioactive Compounds in Medical Applications:

Although radioactive isotopes can cause the problems outlined above, their beneficial effects in therapy and medical diagnosis should be kept in mind. Some of these are given below.

<u>Isotope</u>	<u>Form Employed</u>	<u>Treatment or Diagnosis</u>
Co^{60}	metallic cobalt (Co)	treatment of tumors
Cu^{64}	copper acetate ($\text{Cu}_2(\text{O}_2\text{CCH}_3)_4$)	brain scans for tumors
I^{131}	sodium iodide (NaI)	hyperthyroidism
Tc^{99}	sodium pertechnetate (NaTcO_4)	brain and tumor scans

VI. Chemical Toxicity

A good understanding of environmental control necessitates a good understanding of chemical toxicity. The latter, as it pertains to the problem in question, is presented below. The control or disposal of toxic wastes necessitates both legislation and enforcement. Note that even though legislation is good without enforcement it cannot achieve its goals. *It should be realized that in dealing with toxic waste problems, all parties responsible for the generation of toxic wastes and their disposal must be held accountable.* Although major industry has been cited as the culprit for disposing much of the toxic waste in the environment, *the public and small businesses also contribute.* For example, the Huron River in Southeastern Michigan has been polluted by wastes from municipalities and small businesses rather than by wastes from industrial organizations.

Toxicity

It is difficult to come up with a good test to ascertain the toxicity of a substance. So far only animals such as rats and mice have been used to evaluate the toxicity of

chemicals, and the results thus obtained are assumed to be related and projectable to humans. This assumption may not necessarily be valid, as small animals may metabolize chemicals differently from humans. Nevertheless, this testing can serve as a good guide for toxicity in place of actual evaluation of toxicity on humans. The toxicity of chemicals required by the The Toxic Substance Control Act (TSCA) is evaluated by the following test:

- a. Oral LD₅₀
- b. Inhalation
- c. Skin irritation
- d. Eye irritation

These tests are carried out on rats which weigh from 250-300 grams each, employing three male and three female animals. The individual tests are carried out as follows:

- a. Oral LD₅₀

The term LD₅₀ refers to the lethal dose, that is, the minimum quantity of a substance, orally administered,

that is required to kill 50 percent of the animals tested. LD₅₀ values are given in grams or milligrams of substance per kilogram body weight. By definition (according to law as provided by TSCA), a LD₅₀ value of 5g/Kg is the upper limit for toxicity. A chemical that has an LD₅₀ value of >5g/Kg is not considered toxic. Typical examples and oral LD₅₀ values are:

<u>Compound</u>	<u>Oral LD₅₀ Value</u>	<u>Toxicity</u>
NaCN	15 mg/Kg	Very Toxic
NaCl	3.75 g/Kg	Medium Toxicity
Na ₂ MoO ₄	2.8 g/Kg	Medium Toxicity
Sb ₂ O ₃	>20 g/Kg	Non-toxic
DDT*	113 mg/Kg	Very Toxic

*dichlorodiphenyltrichloroethane

These values refer to handling of the chemicals themselves. No deaths are occurring as a result of inhalation, and skin and eye irritants are to be specified so people have a clear idea of what a chemical can do if it comes in contact with the human body.

It should be noted that toxicity must be principally a matter of solubility. For example, Sb₂O₃, (antimony oxide), which is in the same group in the periodic table

as the very toxic As_2O_3 , (arsenic oxide), is non-toxic according to the law. This non-toxicity can be attributed to its low solubility which causes no problems when it is ingested. However, soluble BaCl_2 is highly toxic to humans, 0.8g being fatal to humans when ingested. Yet, the highly insoluble BaSO_4 is used routinely as a barium enema in X-ray diagnostic work of the gastrointestinal tract.

Different rules, however, apply for the disposal of chemicals in water, i.e., the effects and toxicity on aquatic life must first be tested before their discharge into river, lakes, etc. For example, let us consider two chemicals that have been used as corrosion inhibitors of car, radiator and cooling towers. These are sodium chromate, Na_2CrO_4 , and sodium molybdate, Na_2MoO_4 . Both of these heavy metals are in the same group in the periodic table. Chromate ions contain hexavalent chromium (6+) and are very toxic to aquatic life. Consequently, chromate can no longer be discharged into bodies of water or sewers. However, chromate can first be reduced with Fe^{2+} to trivalent chromium (Cr^{3+}) as $\text{Cr}(\text{OH})_3$. Trivalent chromium is considered to be far less toxic than $[\text{CrO}_4]^{2-}$, and it may be discharged into water or sewers. Even discharge of Cr^{3+} may be banned

in the future. Thus, we see that toxicity depends on the oxidation states of an element. For example, chromium metal in steel, Cr^0 , is not considered toxic. However, zerovalent mercury, Hg^0 , at one time was thought to be so unreactive that it was discharged into the environment. It later was found that Hg reacted with the organic matter in water to form methyl mercury, HgCH_3 , a very toxic compound.

Research leads to important findings:

Na_2MoO_4 , Sodium molybdate has been introduced into the market as a replacement for chromate in corrosion inhibition applications (car radiators and cooling towers). Data had to be provided to the government to show its effect on aquatic life at the levels it would be discharged into the environment. All the usual oral, inhalation and skin and eye irritation studies also had to be conducted. A comparison with chromate was also provided. The test used is called TL_{50} which refers to the toxic dose to fish, that is, the minimum concentration in water of a chemical that will begin to produce toxic effects, including death, to fish. It was found that sodium molybdate is far less toxic than chromates and DDT at the levels specified and it has thus met the required government standards. DDT, as

you may know, is highly toxic even at levels of 0.01 mg/l.

It should be realized that the testing of chemicals is an expensive and time consuming process. For example, obtaining oral LD₅₀ inhalation, skin and eye irritation tests for sodium molybdate required one month to conduct as the behavior of the animals had to be monitored over this time period.

Air Pollution Control

Air pollution control is an important component in the clean-up of our environment. Federal legislation regulates automobile emission pollutants and sulfur oxide emissions from the combustion of fossil fuels. Hydrocarbon emission C_xH_y , are also of concern because they contribute to photochemical smog. Under the Clean Air Act, Natural Ambient Air Quality Standards were supposed to have been met in 1982. They weren't. The deadline was extended to December 31, 1987. They still aren't met. In an attempt to meet ozone standards, some states (e.g., New Jersey, New York) are urging that gasoline volatility be reduced. Others (e.g., Colorado) are combating a CO problem

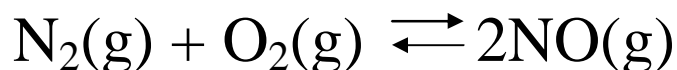
and are urging that gasoline volatility be increased. These air pollution topics are discussed in this document.

I. Cleanup of Automobile Exhaust Emissions

Catalytic converters were introduced in the United States in the 1975 model-year cars. Exhaust passes through the converter and mixes with oxygen which oxidizes carbon monoxide and hydrocarbons to carbon dioxide and water. Hydrogen which is produced in the catalytic converter from reaction of CO with H₂O reduces nitrogen oxides (NO_x) to nitrogen and water. Legislation regulates the quantity of the pollutants, CO, C_xH_y, and NO_x, that can be emitted from moving vehicles (automobiles).

A. Where does the NO_x come from in car exhaust?

The NO_x is formed at the high temperatures (>1200°C) in the combustion chamber of vehicles. The source of the N₂ and O₂ is from air that is drawn into the car's engine.



This reaction is endothermic (requires heat) and therefore occurs more easily at the high temperatures in the engine.

B. Principal Oxides of Nitrogen

NO_x Found in Automobile Exhaust is of two different types:

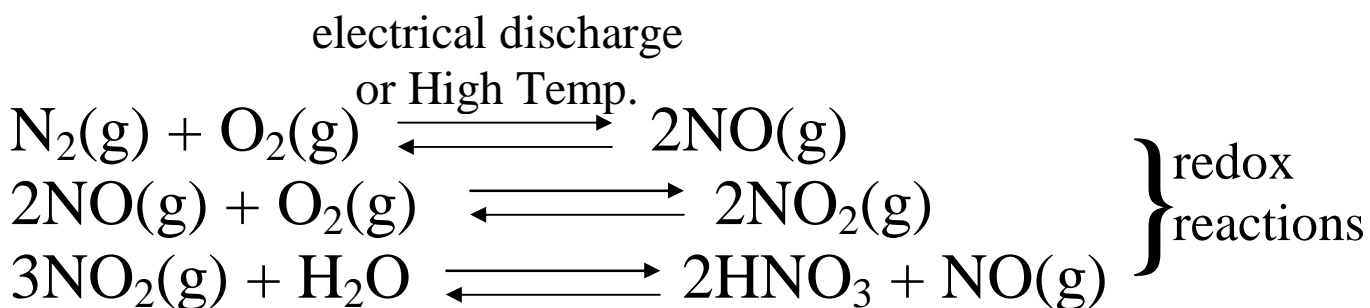
- 1. NO** The colorless **NO (nitric oxide)** molecules react with oxygen to form brown nitrogen dioxide, NO₂. The NO-NO₂ equilibrium is depicted below.



- 2. NO₂** The toxicity of **NO₂ (nitrogen dioxide)** results from its reaction with moisture to yield nitric acid. Lung tissue is attacked when NO₂ is inhaled. Both NO and NO₂, formed by nature during electrical storms, are carried to the ground in the form of nitric acid precipitation. These dilute quantities of

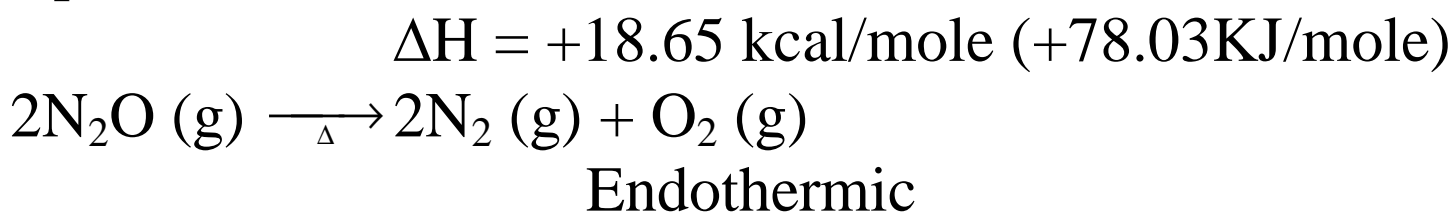
nitric acid act as a fertilizer. Of course, in higher concentrations, nitric acid is harmful and contributes to acid rain.

Reactions to produce NO and NO₂ that are triggered by electricity or heat are:

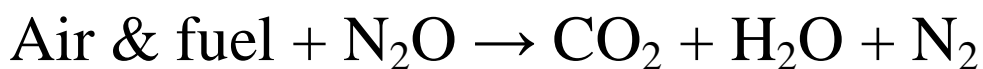


A third Oxide of Nitrogen is Not Found in Automobile Exhaust

3. N₂O In addition to NO and NO₂, there is another oxide of interest, **dinitrogen monoxide or nitrous oxide, N₂O**, also known as laughing gas, which is not found in automobile exhaust. It is relatively nontoxic and is used as an anesthetic. If N₂O is heated too strongly it breaks up into elements according to the equation:



Because N₂O supports combustion, *hot rod and race car drivers sometimes use it to enhance the power output of their engines:*



C. **Three-Way Catalytic (TWC) Converter**

Emission Control Requirements

Prior to 1978 the principal emission control targets had been hydrocarbons (C_xH_y) and CO. In that year, emission standards require the reduction of NO_x in auto exhausts. To understand why control of these pollutants is not easy, consider that a typical auto exhaust mixture is composed of alkanes, alkenes, aromatics, <1% CO, 10% CO_2 , .01% NO_x , 10% H_2O , 2% O_2 , with the remainder being N_2 .

The term **Three-Way Catalytic (TWC) converter** refers to the **simultaneous removal of C_xH_y , CO and NO_x** from auto exhaust. All modern cars sold in the United States are required to have catalytic converters that meet the environment standards and tampering with the converter is prohibited by law. To verify that the standards are met, all new model cars are submitted for testing to the Environmental Protection Agency (EPA) laboratory in Ann Arbor, MI. The converter operates in such a way that at the air/fuel (A/F) ratio of 14.7/1.00, C_xH_y , CO and NO_x are converted into CO_2 , N_2 and H_2O . The required fuel ratio is maintained in

modern combustion engines by very good control of the atomized fuel/air ratio.

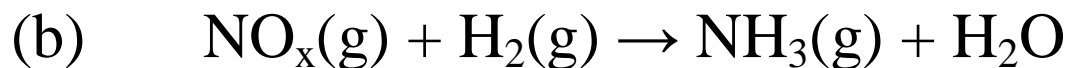
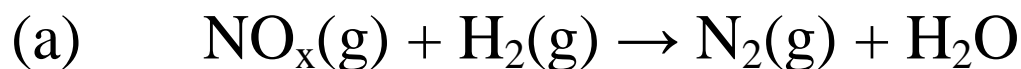
Three–Way catalytic reactions to remove CO, C_xH_y and NO_x:

1. $\text{CO(g)} + \text{O}_2\text{(g)} \rightarrow 2 \text{CO}_2\text{(g)}$
2. $\text{C}_x\text{H}_y\text{(g)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + \text{H}_2\text{O}$
3. $\text{NO}_x\text{(g)} + \text{CO(g)} \rightarrow \text{N}_2\text{(g)} + \text{CO}_2\text{(g)}$
(NO_x is a mixture of NO and NO₂)

The three major by-products are N₂, CO₂ and H₂O.

Note that equations 2 and 3 a,b are unbalanced because they are written in a general way for more than one type of hydrocarbon (C_xH_y) and NO_x compound.

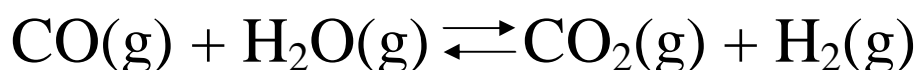
Two side-reactions of the catalytic converter also occur.*



Reaction (a) is desirable as it produces only the safe by-products N₂ and H₂O. However, reaction (b) reduces NO_x too much and leads to undesirable NH₃. A good

catalytic converter will avoid reaction (b) by using a catalyst that does not promote this reaction.

*Note, H_2 for these reactions is produced on the catalyst via the **water gas reaction**:



There are two main types of catalytic converters:

1. **Honeycomb** In this type, the catalytic material is deposited on a honeycomb or grid-like ceramic surface. This ceramic support has the composition $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$, onto which a coat of $\gamma-Al_2O_3$ (a hydroxylated aluminum oxide) is deposited. The catalysts platinum (Pt) and rhodium (Rh), about 0.1% each, are then deposited on the surface of the support.
2. **Spherical** In this type, a spherical rod of $(\gamma-Al_2O_3)$ is used as the support for the catalyst. The catalysts platinum (Pt) and rhodium (Rh), about 0.1% each, are then deposited on the surface of the support.

How does the TWC converter work?

The very hot exhaust gases pass over the catalyst at temperatures between 450-500°C. The common catalysts used in catalytic converters are Rh and Pt in metal form. These are extremely expensive, but are used in such low concentrations on the support are (~0.1%), that is still feasible to use them. Unleaded gasoline must be used with catalytic converters because lead deposits on the catalyst and “poisons” (destroys) it.

II. Removal of NO_x From Smoke-Stack Gases

Combustion of coal and fuel in power plants results in emission of not only SO_2 but also NO_x . Pollution control from such stationary sources is not at an effective level in the U.S. We have already discussed SO_2 pollution and acid rain. We now consider NO_x pollution from stack gases. At present, there are two ways to control NO_x emissions or to remove them from stack gases.

A. Combustion Modification

Combustion modification is practiced in the United States because the NO_x is formed from N_2 and O_2 during the combustion of fossil fuels. Recall that coal, oil, and shale oil contain organic nitrogen which can amount up to 2% N by weight.

Combustion modifications are carried out as follows:

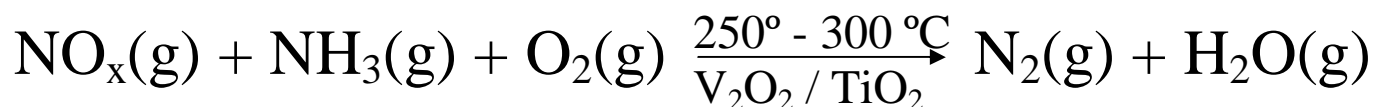
- a) To avoid the combustion of organic (hydrocarbon-containing) nitrogen to NO_x and the conversion of N_2 to NO_2 , both the peak flame and furnace temperatures are reduced.
- b) The time the gases spend at peak temperatures is reduced.
- c) Excess air, and hence excess O_2 is kept from the furnace.

In this manner about 50% NO_x reduction is obtained, but the emitted combustion products contain some CO and hydrocarbons because the burner environment is reducing. Fuel efficiency is also reduced under the “combustion modification” procedure.

B. Catalytic Removal of NO_x

In Japan catalytic removal of NO_x is practiced. The high population density of that country necessitates

such procedures. The catalytic removal of NO_x from stack gases is accomplished as shown by the equation:



Here, a mixture of ammonia and air are used within the specified temperatures range to reduce NO_x to the ppm (parts per million) level. In the greater Tokyo Bay area the NO_x levels are required to remain below 12 ppm at any given time, and the catalytic control insures such levels.

C. Non-Catalytic Removal of NO_x and SO_2

Another “scrubbing” technique has recently been instituted on a commercial basis in Japan in certain instances. For example, NO_x and SO_x ($\text{SO}_2 + \text{SO}_3$) are absorbed in alkaline KMnO_4 solution which is a powerful oxidizing agent.



And and thus are



The KNO_3 and K_2SO_4 are used as fertilizers. The reduced KMnO_4 product, MnO_2 , is then oxidized back to KMnO_4 for reuse.

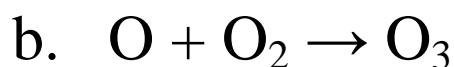
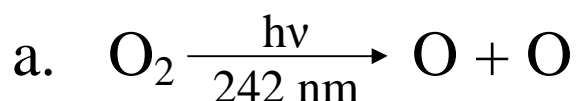
END OF TOPICS DISCUSSED IN CLASS

III. Photochemical Reactions and Ozone

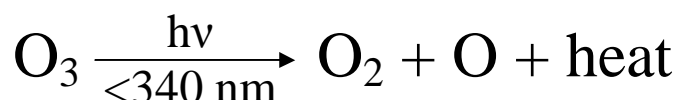
To understand both ozone depletion and photochemical smog reactions we must consider **ozone, a beneficial ingredient at high altitudes in the atmosphere (stratosphere) that screens us from the sun's ultraviolet radiation.**

A. Formation of Ozone

Ozone, O_3 protects us from the intense ultraviolet radiation of the sun by absorbing this high energy radiation. Ozone is formed by the reaction of O_2 with high energy radiation to give O atoms which themselves react with O_2 to give O_3 .



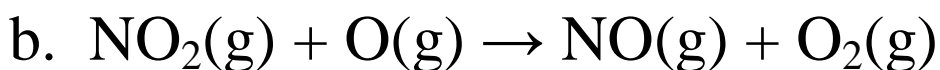
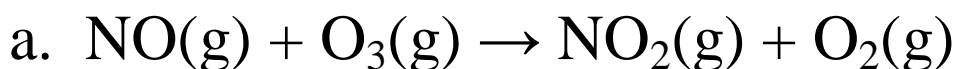
Ozone can decompose by the photochemical reaction below by absorbing lower energy ultraviolet radiation.



B. Ozone Depletion

(1) **Nitric oxide depletes ozone**

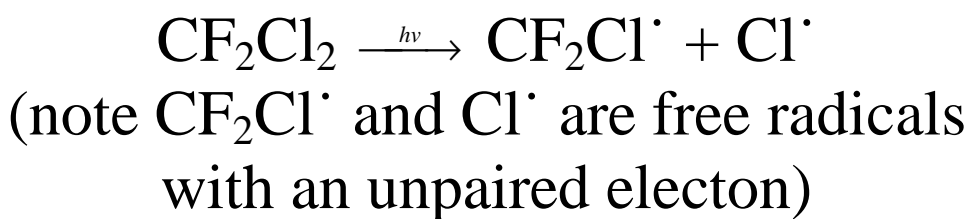
NO put into the atmosphere from the combustion of fuels contributes to ozone depletion as follows:



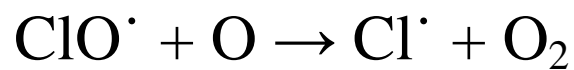
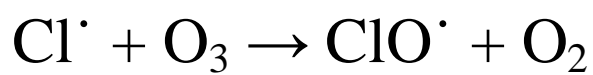
Note that nitrogen oxides are not removed during ozone depletion, but are regenerated.

(2) **Freons deplete ozone**

Freons are put into the atmosphere by aerosol can products and refrigeration unit leakage. Freons are a class of hydrocarbons called chloro, fluoro hydrocarbons. These contribute to the destruction of ozone according to the reactions below:



then ozone destruction occurs as follows:



(the reactive Cl radical is regenerated)

IV. Smog

Photochemical (Los Angeles) smog

London smog

A. London smog

This type of smog results from air-born SO_2 which reacts with moisture to form sulfurous acid and causes lung irritation.

B. Photochemical smog

This type of smog requires the presence of NO_x and ozone; the smog is brown because of the presence of NO_2 .

The ingredients for photochemical smog are:

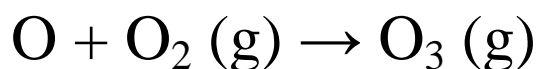
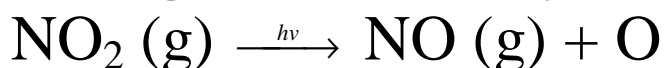
- a. sunlight
- b. NO_x
- c. hydrocarbons

Los Angeles and Mexico City are considered to be the most polluted cities in the world, with Mexico City being the worst example of air pollution. At an 8000 foot high elevation (less oxygen in the air), it is situated in a bowl arrangement that traps pollutants from the estimated population of about 18 million. There is little

environmental control, and photochemical smog impairs visibility considerably.


NO_x results from the combustion of fuels; unburned hydrocarbons from the evaporation of fuels (e.g. gasoline at the gas stations). The following reactions are involved in photochemical smog:

Nitrogen Dioxide Cycle



Note that ozone is produced in this cycle. It is ironic that build-up of ozone is occurring in the lower atmosphere where we don't want it, while at the same time, it is being depleted in the upper atmosphere where we need it.

upper atmosphere too little O_3
too much SO_2 , NO_2 , CO_2
~~haze SO_2/H_2O droplets~~

 ← acid rain

lower atmosphere

PO_3 , NO_x , SO_x , CO_2
too much

Earth

Summary of Air Pollution Control

Chem 362

I. Cleanup of Automobile Exhaust Emissions

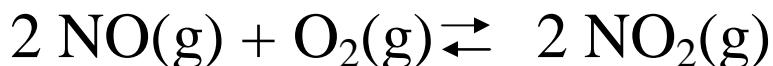
Exhaust passes through the converter and mixes with oxygen which oxidizes CO and hydrocarbons to CO₂ and H₂O. H₂, produced in the catalytic converter from reaction of CO and H₂O, reduces NO_x to N₂ and H₂O.

A. Where does the NO_x come from in car exhaust?



B. Principal Oxides of Nitrogen

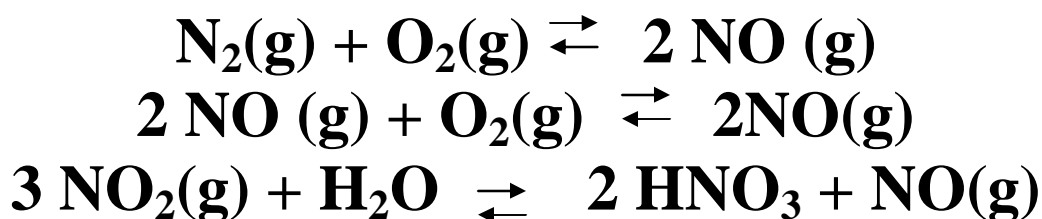
1. colorless NO (nitric oxide)



2. NO₂ (Nitrogen dioxide) is toxic because it reacts with moisture in the lungs to produce nitric acid.

These two oxides when produced by nature during electrical storms and carried to the ground by rain act as a fertilizer.

Know the following reactions that produce NO and NO₂ and are triggered by electricity or heat:



A third oxide or nitrogen NOT FOUND in Automobile Exhaust.

- 3. N₂O (dinitrogen monoxide or nitrous oxide), ‘laughing gas.’** Upon heating, N₂O decomposes to N₂(g) and O₂(g); it supports combustions, and **hot rod and race car drivers sometimes use it to increase the power output of their engines.**

C. Three Way Catalytic (TWC) Converter

The **TWC** refers to the **simultaneous removal of C_xH_y (hydrocarbons), CO, and NO_x** from automobile exhaust. Efficiencies are >80% if the air/fuel ratio is between 14.6/1 and 14.7/1. An O₂ sensor is in the exhaust stream.

Know the following TWC reactions:

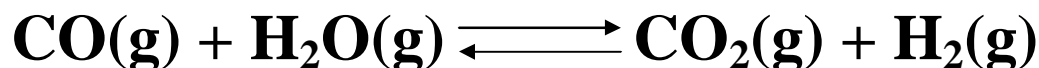
1. $2 \text{CO(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2 \text{CO}_2\text{(g)}$
2. $\text{C}_x\text{H}_y\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{H}_2\text{O (g)}$
3. $\text{NO}_x + \text{CO(g)} \rightleftharpoons \text{N}_2\text{(g)} + \text{CO}_2\text{(g)}$

Know the two side reactions of the catalytic converter:

- (a) $\text{NO}_x\text{(g)} + \text{H}_2\text{(g)} \rightleftharpoons \text{N}_2\text{(g)} + \text{H}_2\text{O}$
- (b) $\text{NO}_x\text{(g)} + \text{H}_2\text{(g)} \rightleftharpoons \text{NH}_3\text{(g)} + \text{H}_2\text{O}$

Reaction (a) is desirable; reaction (b) illustrates excessive reduction and is undesirable.

$\text{H}_2\text{(g)}$ is produced on the catalyst by the **water gas reaction**:



Types of catalytic converters:

1. **Honeycomb** – a ceramic support with $\gamma\text{-Al}_2\text{O}_3$ on which are Pt and Rh.
2. **Spherical** – $\gamma\text{-Al}_2\text{O}_3$ rods with deposits of Pt (platinum) and Rh(rhodium).

Understand that the Pt and Rh are catalysts; they operate at 450-500°C.

Why must **unleaded** fuels be used?

II. Removal of NO_x From Smoke-Stack Gases

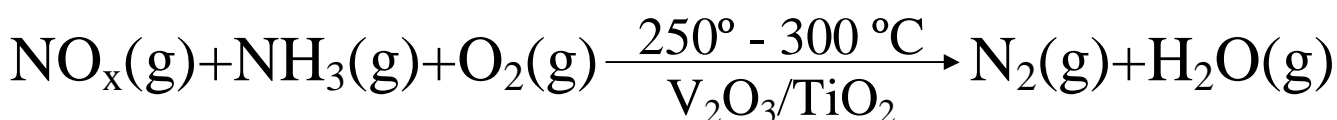
Recall: Power plants emit NO_x and SO₂.

A. Combustion Modification (method reduces fuel efficiency)

Fossil fuels contain up to 2% by wt. N; recall: $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{NO}(\text{g})$

- (a) peak flame and furnace temperature are reduced.
- (b) time gases are at peak temperature are reduced.
- (c) excess air (O₂) is kept in the furnace.

B. Catalytic Removal of NO_x:



C. Non-Catalytic Removal of NO_x and SO_x

Absorb the NO_x and SO_x in **alkaline KMnO₄** → **KNO₃(s)** and **K₂SO₄(s)**. These products are used as fertilizers; the other product, MnO₂, can be oxidized back to KMnO₄. This method is “*environmentally smart*.”

Environmental Chemistry

I. A. Natural Greenhouse Effect & Gases

CO_2 , CH_4 , N_2O provide a *natural insulating effect* of earth's atmosphere.

Screen energy from sun; absorb radiated by earth and **reradiate** it back to earth.

B. Unnatural Greenhouse Gases – Global Warming

Burning of *fossil fuels* (coal & oil) produces CO_2 , upsetting the natural balance between production & uptake by plants (photosynthesis) and oceans ($\text{Mg/CaCO}_3(\text{s})$). Oceans take up $\text{CO}_2(\text{g})$ very slowly. Continued addition of CO_2 may increase earth's temperature, causing polar ice caps to melt in addition to producing other climatic changes.

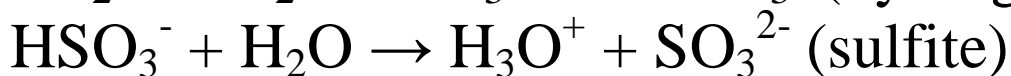
II. Sulfur Dioxide Emissions

Fossil fuels (oil/gas/coal) contain large amounts of sulfur. Why? North Sea oil (1% S); Middle East Oil (4-5% S).

80% of SO_2 put into atmosphere comes from power plants: $\approx 26.5 \times 10^6$ ton/yr.

III. Acid Rain

Results when SO_x ($\text{SO}_2 + \text{SO}_3$) and NO_x ($\text{NO} + \text{NO}_2$) react with H_2O .



SO_x and NO_x form stable aerosols in the atmosphere and move over the globe. Lakes become polluted because of acid rain. Some lakes at pH 4.0 support aquatic life; others don't. Aluminum in lakes which results from acidification prevents fish from breathing. Lakes buffered with (Ca/Mg) CO_3 recover from acid rain; those not buffered do not.

IV. Combustion of Fossil Fuels (methane, coal, oil)

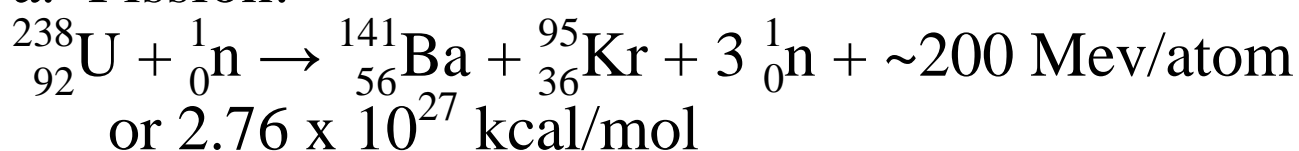
1. Methane: $\text{CH}_4 + 2 \text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{CO}_2 + \text{heat}$.

$\Delta H^\circ = -192$ kcal of heat released per 16 g of CH_4 ; a 'clean fuel,' but give CO_2 .

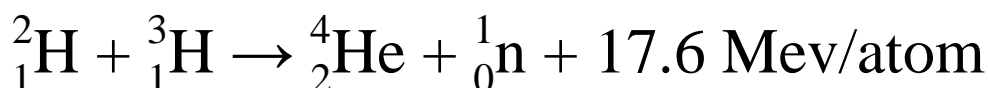
V. Nuclear Fuels & Radioactive Compounds

A. Nuclear Fuels

a. Fission:



b. Fusion:



On a per mole basis, fission and fusion release orders of magnitude more energy than does methane, but there are potential problems:

- leakage of radioactive species from nuclear reactors
- potential for malignancies due to radioactivity
- difficulty in disposing of nuclear wastes.

B. Radioactive Compounds in Medical Applications

Some radioisotopes have beneficial medical effects in therapy and diagnosis.

VI. Chemical Toxicity

Toxic wastes:

“..parties responsible for the generation of toxic wastes and their disposal must be held accountable.”

Toxicity: Animals such as rats and mice are used to evaluate toxicity of chemicals, and the results are **assumed** to be projectable to humans. Toxicity of chemicals required by the Toxic Substance Control Act is evaluated by the tests:

- Oral LD₅₀

- Inhalation

- Skin irritation

- Eye irritation

Oral LD₅₀ – lethal dose: the minimum quantity of a substance, orally administered, that is required to kill 50% of the animals tested.

Units: grams or milligrams/kilogram of body weight.

LD₅₀ > 5g/Kg; non-toxic.

NaCN: $LD_{50} = 15 \text{ mg/Kg}$; NaCl: $LD_{50} = 3.75 \text{ g/Kg}$;
DDT: $LD_{50} = 113 \text{ mg/Kg}$

BaCl₂ toxic, yet BaSO₄ is used as an enema in X-ray diagnostic work. Why? Cr^{VI} is very toxic, but Cr^{III} may be discharged into sewers. Why? Na₂MoO₄ safely replaces Cr^{VI} as a corrosion inhibitor in antifreeze solutions.

SCIENCE'S COMPASS

found in cells transformed by certain oncogenes (9, 10).

The gene encoding TAF_{II}250 was identified long before any clear evidence emerged for its role in transcriptional regulation. A wild-type copy of the gene—*CCG1* (cell cycle gene 1)—from normal cells rescued the G₁ phase arrest of cells bearing a *CCG1* point mutation (11). It turns out that the protein encoded by *CCG1*, TAF_{II}250, is a critical subunit of TFIID and integrates interactions between transcription factors and various TAF_{II}s, enabling their communication with TBP, the DNA binding component of TFIID (2). The discovery that TAF_{II}250 possesses both acetyltransferase and kinase activities (12, 13) suggests a catalytic as well as a structural role for this subunit in gene expression. Intriguingly, cells with mutations that affect the HAT activity of TAF_{II}250 become arrested in late G₁ of the cell cycle, suggesting that TAF_{II}250 regulates the expression of genes involved in cell proliferation (14).

The Pham and Sauer results are unexpected because they point to an even greater diversity in the enzymatic capabilities of TAF_{II}250 than previously surmised. Al-

though ubiquitination is most frequently associated with degradation of proteins through the proteasome pathway (15), ubiquitinated H2A and H2B are known to be enriched in transcriptionally active chromatin (16, 17). Pham and Sauer show that the ubiquitin-conjugating activity of TAF_{II}250 is associated with H1 ubiquitination in *Drosophila* embryos. Their data suggest that ubiquitination alone, or in combination with the modification of other chromatin-associated proteins, may alleviate repression of transcription by H1. This raises several intriguing questions: To what extent do the HAT and kinase activities of TAF_{II}250 influence H1 ubiquitination and vice versa? Do distinct combinations of different histone modifications form a code that influences which sets of genes are transcribed (6, 18)? Identification of the H1 sites that are ubiquitinated by TAF_{II}250 may reveal synergy between H1 phosphorylation and H1 ubiquitination.

Other important issues raised by this work include determining the effect of H1 ubiquitination on chromatin structure, whether ubiquitination influences the proteolytic turnover of H1 in a locus-specific manner, and whether H1 is ubiquitinated in other organisms. Chro-

matin remodeling varies with the different stages of the cell cycle (19). Thus, the initial description of TAF_{II}250 as a cell cycle regulator begs for a careful analysis of the cell cycle dependency of H1 ubiquitination and of the HAT and kinase activities of this important TFIID subunit. Even though more work is required to elucidate the importance of H1 ubiquitination, this addition to the list of TAF_{II}250's chromatin modifying activities provides further evidence for the key part played by this molecule in gene transcription.

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PERSPECTIVES: ATMOSPHERIC CHEMISTRY

The NO₂ Flux Conundrum

Manuel T. Lerdau, J. William Munger, Daniel J. Jacob

Striking progress has recently been made in understanding the central role of nitrogen oxide radicals, NO_x, in atmospheric processes. NO_x is implicated in the formation of acid rain, tropospheric ozone (the principal toxic component of smog and a greenhouse gas), and the hydroxyl radical

(the main atmospheric oxidant responsible for the destruction of many pollutants). Atmospheric models have had some success at reproducing regional and continental acid deposition patterns, ozone profiles, and hydroxyl radical concentrations on the basis of estimated NO_x emissions (1–3). However, atmospheric and biological studies have yielded seriously incompatible results regarding the role of vegetation as a sink or source of NO_x. This is an important problem because we must understand NO_x

emission processes to be able to predict future environmental impacts (4–6).

The major known sources of NO_x are fossil fuel combustion, biomass burning, microbial activity in soils, and lightning. Globally, these sources produce a total of 30 to 50 teragrams (Tg) of nitrogen year⁻¹ of which microbes in soils contribute 5 to 10 Tg year⁻¹. The vast majority of NO_x is released as nitric oxide, NO, which converts to nitrogen dioxide, NO₂, within minutes by reaction with ozone and peroxy radicals. NO₂ is recycled to NO by photolysis. This cycle is at the heart of tropospheric ozone formation. Typical NO/NO₂ concentration ratios in surface air are 0.2 to 0.5 in the daytime and zero at night when no NO₂ photolysis takes place. Over time scales of hours to days, NO_x is converted to nitric acid and nitrates, which are removed by rain and dry deposition and contribute to acidification and excess nutrients in sensitive ecosystems.

NO_x is also removed directly from the air through uptake of NO₂ by foliage. This process extracts NO_x from the atmosphere and also removes soil-derived NO_x from the air before it can be exported to the atmosphere. The efficiency of the latter process is crucial for determining the NO_x concentration

above landscapes dominated by biological activity. A quantitative analysis of this effect was made by Jacob and co-workers (7, 8) using data from an Amazonian forest site during the wet season. The authors modeled observed NO_x concentrations in the canopy air with a one-dimensional atmospheric transport and chemistry model constrained by measured NO soil emission fluxes and estimated that only 25% of the NO_x emitted by soils is ventilated to the atmosphere. Globally, the fraction of soil-derived NO₂ ventilated out of canopies has been estimated at 50 to 80% (9, 10) by extrapolating Jacob and co-workers' results to canopies of different leaf area indices.

The kinetics of NO₂ uptake by plants have been studied by biologists interested in NO₂ exchange mechanisms and the impact of NO₂ on plant function. In these bottom-up studies, leaf-level exchange of NO₂ is measured across a range of concentrations, and a "compensation point" is calculated assuming first-order uptake kinetics. At ambient concentrations below the compensation point, the plant canopy is a net source of NO₂ to the atmosphere, whereas at concentrations above this point, it acts as a net sink. Most studies of leaf-level NO₂ exchange have shown compensation points between 1 and 3 parts per billion by volume (ppbv) (11–15). These results contradict those of Jacob and co-workers (7, 8), who found that at NO₂ concentrations as low as 0.2 to 0.4 ppbv in the canopy air, rapid net uptake of NO₂ by the leaves was

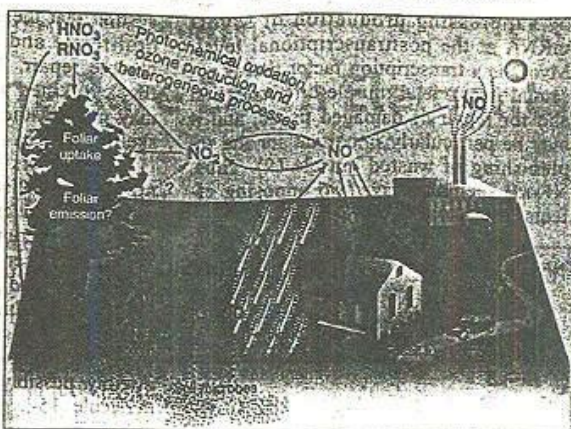
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www.sciencemag.org/cgi/content/full/289/5488/2291

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SCIENCE'S COMPASS

needed to reconcile the measured NO soil emission fluxes with the NO concentrations measured in the canopy air. Because of low sensitivity of the analytical methods available for bottom-up studies, it has been difficult to obtain data at the low concentrations typical of ambient nonurban NO₂ concentrations (0.05 to 1 ppbv) and thus to confirm the assumption of first-order uptake kinetics and the existence of a compensation point.

The discrepancy between top-down and bottom-up approaches has important implications for our understanding of both atmospheric chemistry and plant function. Atmospheric NO₂ concentrations in nonurban surface air are typically much less than 1 ppbv, and the NO₂ compensation points determined in the bottom-up studies would thus imply that vegetation canopies are large NO₂ sources, with 24-hour average NO₂ emission fluxes on the order of 2×10^{10} molecules cm⁻² s⁻¹ (16). In comparison, soil emissions of NO are typically 10^8 to 10^{11} molecules cm⁻² s⁻¹ (9). Inclusion of such a large vegetation source in atmospheric chemistry models would require a hitherto unrecognized NO₂ sink to balance the budget.



Sources and sinks. This scheme shows the main NO₂ sources and sinks. The magnitude of NO₂ uptake by vegetation is not known, and the existence of an NO₂ source from vegetation is contentious.

Resolving the differences in sign and magnitude of leaf-atmosphere NO₂ exchange will require both top-down and bottom-up approaches. Leaf-level measurements will have to be made with techniques that are sensitive at very low NO₂ concentrations. More studies of the key metabolites involved with NO₂ assimilation are needed. NO₂⁻, NO₃⁻, and chloroplast pH measurements during nitrate reduction may help explain the source of NO₂ within leaves. Combined with quantitative biochemical modeling (17), such measurements will improve the accuracy of NO₂ concentration-uptake curves and help determine the true value of the NO₂ compensation point—if such a point does indeed exist. As

for top-down approaches, simultaneous measurements of NO fluxes from soils, NO₂ fluxes across leaf surfaces, NO₂ fluxes above canopies, and NO_x concentrations in canopy air across a range of ambient NO₂ concentrations are necessary to test the models developed from controlled environment leaf-level studies. Without such measurements, the role of leaf-level exchange and the importance of plant physiological regulation for NO₂ exchange between the surface and the atmosphere cannot be quantified. This issue must be resolved to close the budget of this important atmospheric species.

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PERSPECTIVES: BIOMEDICINE

Protein Loss in Cancer Cachexia

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Patients with chronic diseases such as AIDS or cancer (particularly those with tumors of the pancreas, stomach, colon, and lung) often experience a life-threatening muscle wasting syndrome known as cachexia. Cachexia is characterized by a dramatic loss of triglycerides from adipose tissue and proteins from skeletal muscle. Although it superficially resembles starvation, it is refractory to nutritional intervention. Loss of skeletal muscle mass results in lowered mobility and, hence, a poorer quality of life for the patient, while erosion of respiratory muscle eventually leads to death from pneu-

monia. Cachexia is associated with reduced survival time irrespective of tumor mass or the presence of metastases, and it also interferes with cancer therapy. Knowledge of the molecular pathways leading to cachexia is required if an effective treatment is to be developed. The report by Guttridge et al. (1) on page 2363 of this issue identifies the master transcription factor NF- κ B as an inhibitor of skeletal muscle cell differentiation and a mediator of cytokine-induced muscle wasting in mice. These findings provide potential new targets for therapeutic intervention to treat cachexia.

Loss of skeletal muscle proteins reflects an imbalance between the rate of protein breakdown (catabolism) and the rate of resynthesis of depleted proteins.

The ubiquitin-dependent proteolytic pathway breaks down most skeletal muscle proteins in a variety of wasting conditions (2). In this pathway, proteins are marked for degradation by the attachment of ubiquitin, which requires the activity of enzymes E1, E2, and E3. The polyubiquitinated protein is then degraded in a multisubunit complex, the 26S proteasome—a tubelike structure consisting of a stack of four rings, two outer α rings and two inner β rings (see the figure). The proteasome releases short oligopeptides containing six to nine amino acid residues, which are rapidly degraded into amino acids by cytosolic peptidases.

When ubiquitin-proteasome proteolysis is accelerated in muscle, usually there is a concurrent increase in the production of mRNAs encoding enzymes in this pathway (2). Preventing the transcription of just one proteasome α subunit (C2) with antisense oligonucleotides reduces the number of proteasomes, proteolytic activity, and consequently protein degradation (3). Recent

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