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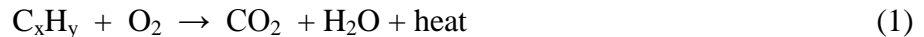
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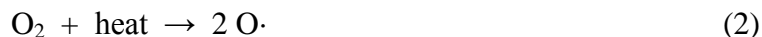
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INTRODUCTION

Automobile engines convert the energy stored in chemical bonds into mechanical energy through the controlled combustion of gasoline (hydrocarbons, C_xH_y) in air:

$$C_xH_y + O_2 \rightarrow CO_2 + H_2O + heat \tag{1}$$

When there is the correct balance of O_2 and hydrocarbons in the combustion chamber (i.e., under "lean" conditions), complete combustion occurs and CO_2 and H_2O are emitted in the exhaust. When the mixture is not in balance, such as the case when there is too much fuel and not enough oxygen (i.e., under "rich" conditions), combustion is incomplete and the exhaust can contain CO and excess hydrocarbons. Since both nitrogen and oxygen are present in air used for combustion, the following reactions may also take place within the engine, especially when the combustion temperature is high:

$$O_2 + heat \rightarrow 2 O\cdot \tag{2}$$
$$O\cdot + N_2 \rightarrow NO\cdot + N\cdot \tag{3}$$
$$N\cdot + O_2 \rightarrow NO\cdot + O\cdot \tag{4}$$
$$2 NO\cdot + O_2 \rightarrow 2 NO_2 \tag{5}$$

As a result, nitrogen oxides ($NO_x = NO + NO_2$) are also present at high concentrations in car exhaust. Typical untreated car exhaust may contain CO concentrations of 1–2% by volume, unburned hydrocarbons levels between 500-1000 ppm and NO_x levels between 100-3000 ppm. The unit of ppm, or parts-per-million, is called a mixing ratio. In fact, scientists prefer to measure the amount of trace pollutants such as NO_x or ozone in the air in terms of ppm or even parts per billion (ppb), which are defined as follows:

> 1 ppm = 1 molecule reported per 1,000,000 molecules of other gases in air
> 1 ppb = 1 molecule reported per 1,000,000,000 molecules of other gases in air

With 10 million cars in the South Coast Air Basin alone, the health of humans, agriculture, and natural places depends on our ability to reduce or eliminate emissions of toxic gases such as NO_x, CO and hydrocarbons from automobiles. One of the consequences of all these pollutants is the occurrence of smog in urban areas such as Los Angeles. Photochemical smog is the brown, noxious haze surrounding downtown Los Angeles on a summer day that obscures the view of the San Bernardino Mountains. The typical conditions for smog to develop are:

1. A lot of sunshine
2. Warm air (T > 290 K or 63 °F)
3. Sources of NO_x, CO and hydrocarbons (i.e., combustion exhaust of automobiles and industry)

4. A stable air mass (i.e., a city surrounded by mountains) with the possibility of having an inversion layer that traps gases close to the ground

Los Angeles satisfies all these requirements. One of the most toxic components of smog, and the one that makes breathing difficult for children playing outside on smoggy days, is ozone (O_3). It is formed from a series of chain reactions that are initiated by sunshine and involves free radicals, hydrocarbons and NO_x from automobiles. The concentration of ozone in clean air is around 0.02-0.04 ppm (or 20-40 ppb). Smoggy air can contain considerably more ozone, and 0.1 ppm is quite typical for the Los Angeles area today. In the past, ozone concentrations in L.A. were known to reach values as high as 0.7 ppm. For reference, the air quality standard for ozone today is 0.07 ppm, set by the California Air Resources Board (ARB). The standards are defined as the highest average concentration of ozone that should not be exceeded during a given interval of time.

Automobile emissions have a huge impact on human health and the well-being of our planet. Not only do they lead to elevated ozone levels, but the CO emitted by engines is toxic. Also, both CO_2 and ozone are greenhouse gases. After the link was made between automobiles and air pollution, and after overcoming strong opposition from the automobile industry, regulations to control automobile emissions were finally enacted in the U.S. when Congress passed the Clean Air Act in 1970. Since then, the Environmental Protection Agency (EPA) has established emission standards that automobile manufacturers must abide by when producing cars, and these regulations have become more stringent over time as pollution abatement technology has improved. California and its air pollution regulation body, the Air Resources Board (ARB) has set yet more stringent emission standards for passenger cars; they are listed in Table 1. The most effective way to meet the emission requirements of the Clean Air Act and those of the ARB has been through the implementation of catalytic converters. These days, ULEV and ZEV vehicles are also possible through recent advances in hybrid, fuel-cell and battery technology. In addition, cars in California and many other States make car registration contingent upon a car's ability to pass a "Smog Check" that ensures CO, hydrocarbon, and in some cases, NO_x levels in car exhaust are below the regulated levels.

TABLE 1: Summary of California Emission Standards for Passenger Cars.*

Category	NMOG	CO	NO_x
TLEV	0.125	3.4	0.4
LEV	0.075	3.4	0.2
ULEV	0.040	1.7	0.2
ZEV	zero	zero	zero

Abbrev.: LEV = low emission vehicle; T = transitional; U = Ultra; Z = zero; NMOG = non-methane organics. *Units are in *grams per mile*

The catalytic converter is located under the automobile between the engine and the muffler (Figure 1). When the car is first started (i.e. "cold start"), the catalytic converter is cold and the catalyst does not efficiently remove NO_x and CO from the exhaust. As the engine warms up, the exhaust warms the catalytic converter to a high enough temperature to initiate the catalytic reactions that remove pollutants. The catalytic reactions occur heterogeneously (i.e. when

gaseous combustion products adsorb onto the surface of a ceramic monolith and react with the various metal atoms present there) and convert toxic gases into less harmful chemicals.

The active components of catalytic converters are precious metals such as Pt, Pd, and Rh dispersed on the high surface area ceramic monolith that is shaped like a honeycomb (see Figure 2). The honeycomb support can be 10 inches in diameter, 7 inches long, have between 10-500 cells per square inch, and is held inside a metal housing (you will have an opportunity in class to take a catalytic converter apart). The honeycomb structure means that exhaust gases travel through the converter at the fastest possible rate while at the same time hitting a lot of catalyst-covered surface on their way out. This design aims at maintaining fuel efficiency and preventing a loss of power that would happen if the exhaust gases build up pressure going through the converter.
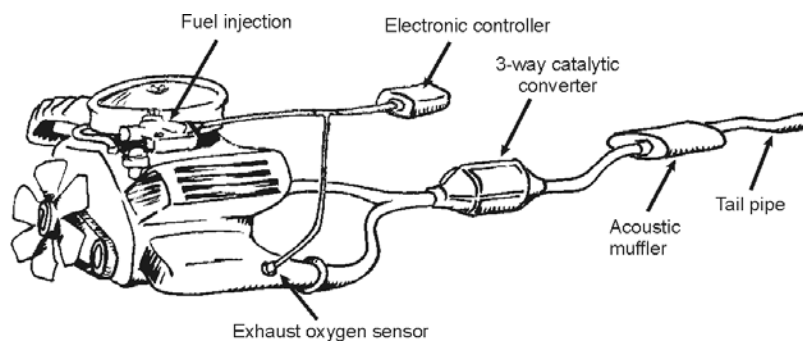

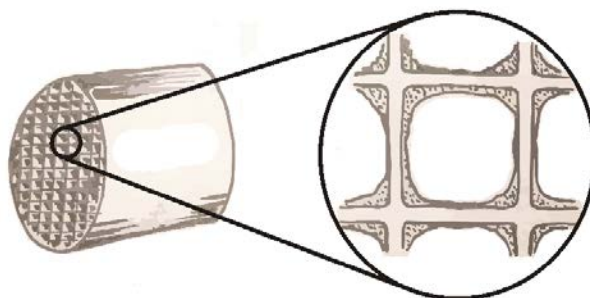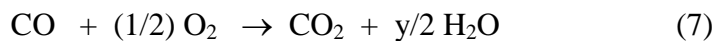**Figure 1.**   Example of the exhaust pathway in the underbody of an automobile.

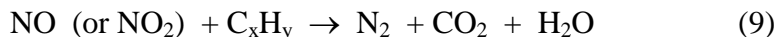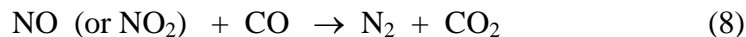**Figure 2.**   Left: Drawing of a $(MgO)_5 \cdot (Al_2O_3)_2 \cdot (SiO_2)_5$ ceramic monolith used as a support for the catalysts. Right: A close up of a layer of high surface area Al_2O_3 (the "wash coat") impregnated with Rh, Pt and Pd catalysts (dotted regions).

What is actually happening in a catalytic converter? In what is known as a three-way catalyst (TWC), hydrocarbons and CO are *oxidized* to CO_2 and H_2O:

$$C_xH_y \;+\; (1 + y/4)\, O_2 \;\rightarrow\; x\, CO_2 \;+\; y/2\, H_2O \qquad\qquad (6)$$

$$CO \;+\; (1/2)\, O_2 \;\rightarrow\; CO_2 \;+\; y/2\, H_2O \qquad\qquad (7)$$

and NO_x is *reduced* to harmless N_2 (note these reactions are intentionally unbalanced because the mechanism of catalysis is very complex)

$$NO \ (\text{or } NO_2) \ + \ CO \ \rightarrow \ N_2 + CO_2 \qquad\qquad (8)$$

$$NO \ (\text{or } NO_2) \ + C_xH_y \ \rightarrow \ N_2 \ + CO_2 \ + \ H_2O \qquad\qquad (9)$$

The metals and metal oxides present in the ceramic monolith act to adsorb both NO_x and O_2, and then break the normally very strong N–O or O–O bonds. On the surface, the resulting oxygen atoms react with CO or hydrocarbons, while N atoms recombine to form N_2. The whole system is catalytic, i.e., during a single catalytic cycle the metal species do not themselves permanently change their identity, but through their interaction with the reactants, serve to reduce the energy barrier (Activation Energy, E_a) to the reaction and speed the reaction up to form more benign gases.

Two conditions must be satisfied for the converter to work properly. First, the temperature of the catalyst must be high enough. This stems from the relation between the temperature and the rate of a chemical reaction, as described by the Arrhenius equation:

$$k = A \exp (-E_a/RT)$$

where k is the rate constant of the reaction, A is the pre-exponential factor, and E_a is the activation energy for the reaction. The second requirement for the catalytic converter to work properly is that the engine combustion chamber must be operated close to the stoichiometric air-to-fuel ratio. This is because there is a narrow range of air-to-fuel ratios in which both NO_x reduction and CO/hydrocarbon oxidation readily occur on the surface of the catalytic converter simultaneously. If there is too much O_2 present, the NO_x reduction does not occur. Conversely, if there is not enough O_2 present, the CO/hydrocarbon oxidation doesn't happen. This fine balance to keep the gas mixtures in the optimum range is continuously adjusted by an oxygen sensor and engine feedback system placed before the catalytic converter in the exhaust manifold.


BACKGROUND

The goals of this experiment are to measure quantitatively the concentration of NO_x in the exhaust of your vehicle using UV/VIS Spectroscopy, and to study the efficiency of your automobile's catalytic converter to decrease NO_x emissions to the atmosphere. We will sample exhaust from the tail pipe of the vehicle immediately at startup and then again after the car has had a chance to warm up for 10 minutes. Each team member will collect one or more exhaust samples to determine the amount of nitrogen oxides present in the gas stream using a chemical indicator.

The Chemical Indicator for NO_x in Exhaust. NO_x at ppm levels can be determined using Ultraviolet-Visible (UV/VIS) Spectroscopy after it is converted into a brightly colored indicator dye in aqueous solution. In solution, NO and NO_2 undergo the following reactions to form nitrous acid (HONO):

$$4 \ NO + O_2 + 2 \ H_2O \rightarrow 4 \ HONO \qquad\qquad (10)$$

$$2 \ NO_2 + H_2O \rightarrow HONO + HNO_3 \qquad\qquad (11)$$

Nitrous acid reacts with sulfanilic acid and N-(1-naphthyl)-ethylenediamine to form an azo dye:

purple azo dye
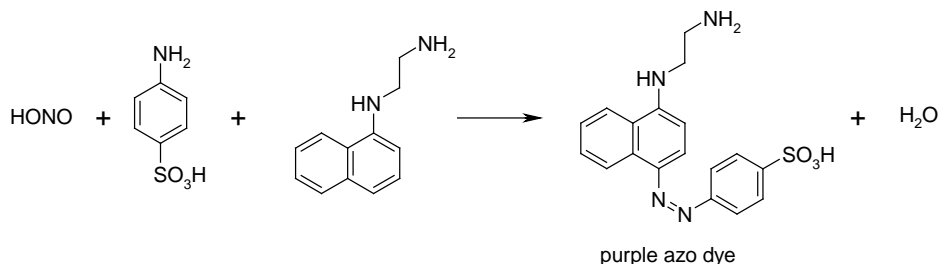
    The concentration of this purple-colored molecule can be easily determined from its absorption band at 550 nm using a UV/VIS spectrophotometer.

Ultraviolet-visible (UV/VIS) Absorption Spectroscopy. The absorption spectrum of a molecule is obtained by measuring the decrease in light intensity passing through the sample (compared to a "blank") as a function of wavelength:

ABSORPTION
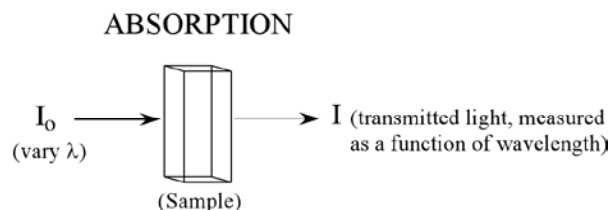
    According to the Beer-Lambert law, the intensity of the transmitted light, I, is related to the initial intensity, I_o, as $I = I_0 \times 10^{-A}$, where A is called absorbance. For sufficiently diluted samples, absorbance is directly proportional to concentration (C) of the analyte and path length (l, in cm) of the sample holder, as shown below:

$$A = \varepsilon l C$$

    The proportionality constant, ε, is called molar absorptivity or molar extinction coefficient, and it is usually determined from the slope of a plot of absorbance against concentration at a known path length. Each molecule is characterized by a unique dependence of ε on the absorption wavelength. This plot can also be used to determine the concentration of an unknown solution.

    The spectrophotometer you will be using is called a double beam spectrophotometer. The light beam is split into two separate beams, and each beam passes through a cuvette. The reference cuvette contains the "blank" solution, in this case the indicator solution. The sample cuvette contains one of the nitrite standards or the exhaust sample solution. Because the cuvettes are not exactly alike, the instrument software has the ability to perform a "baseline correction," which corrects for differences in the amount of light that passes through the two cuvettes at each

wavelength. To do this, make sure both cuvettes contain the blank solution and click the baseline button in the software. The instrument will scan through the wavelength range and measure the amount of light that passes through each cuvette at each wavelength. It will then automatically correct for any differences, so that a blank solution in the sample cuvette will always have an absorbance of 0.

EXPERIMENTAL PROCEDURE

Note: Detailed instructions on the start-up, use, and shut down of the Jasco V-530 UV/VIS spectrometer are provided in the handout near the machine in the lab; please read them carefully before beginning with the experiment. Your TA will help you operate the computer software.

CAUTION!! You will carry out sampling in a potentially busy parking lot. Please be aware of passing vehicles and make sure to stay a safe distance from them as you carry out this experiment. You will be sampling exhaust from a running vehicle. The vehicle should be in park or neutral gear with the parking brake engaged before it is started. Please keep a safe distance from the car as it starts. When sampling exhaust, make sure the tail pipe is not hot before sampling. A hot tail pipe can cause serious burns to the skin. This may be especially important when sampling exhaust after the car has warmed up for 10 minutes. Everyone must wear gloves and protective eyewear during sampling, as well as back in the laboratory.

I: Preparation of the indicator solution

1) Tare a small beaker and measure ~ 2.50 g of sulfanilic acid in it. Quantitatively transfer the solid to about 350 mL of nanopure water in a 500 mL volumetric flask and swirl until dissolved. This could take up to 30 minutes, so go through the Prelab with the T.A. and then start preparing the calibration standards (part II) during this time.

2) Once the acid is dissolved, add 70 mL of glacial acetic acid and dilute to almost 500 mL. As before, quantitatively transfer ~ 0.01 g of *N*-(1-naphthyl)-ethylenediamine dihydrochloride (NEDA) to the flask and swirl.   Dilute to the mark with nanopure water, and invert to mix. Cover the flask with aluminum foil to protect the solution from light.

II: Preparation of the calibration standards

1) A sodium nitrite stock solution containing approximately 1000 μg/mL of NO_2^- has been prepared for you. Record the exact mass of $NaNO_2$ contained in the solution and the volume of the solution from you TA: **mass: _____   flask V: _____**

     Using a 1000 μL micro-pipette, transfer 125 μL (0.125 mL) of this solution to a 25 mL volumetric flask and dilute to the mark with nanopure water to make a solution containing around 5 μg/mL NO_2^-.

2) Transfer 250, 500, 1000, and 2000 μL of the diluted NO_2^- solution, respectively, to four 25 mL volumetric flasks using micro-pipettes. Dilute to the mark with the ***indicator solution***. This should make solutions containing approximately 0.05, 0.1, 0.2, and 0.4 μg/mL NO_2^-.

III: Collection of exhaust samples

1) Obtain five 30 mL syringes with valves and aluminum foil to cover them later, a 250 mL beaker, a thermometer, a marker pen, a funnel, and two screw cap 250 mL Erlenmeyer flasks with about 200 mL of indicator solution in each. Mark the plunger of each syringe to indicate when 12.5 mL of material has been drawn into the syringe (this will help in step 4).

2) Be sure that all people who are not operating the car are neither standing in front nor in back of the vehicle. For the person who is operating the vehicle, check to make sure the car is in park or neutral and that the parking brake is engaged before starting it. Stand out of the way while one member of your group starts the car.

3) Once the car is running, rev the engine to 2000 rpm, place a funnel on a syringe and place into the tailpipe to pull exhaust into the syringe up to 30 mL and empty the syringe. Do this twice to flush the syringe.

4) Draw up 12.5 mL of indicator solution into the syringe. Insert the syringe with funnel again into the tailpipe of the car and draw in exhaust until the total volume reaches 30 mL. Close the valve on the syringe, cover the syringe with aluminum foil and shake the syringe vigorously for a few seconds. Label the syringe as "cold" or "hot" and the car model.

5) Take the temperature of the air near the exhaust pipe ("cold"): T_{cold} = _____ ^{o}C

6) Repeat steps 3-5 with a new syringe after the car has warmed up for 10 minutes. Regard all safety issues mentioned above and take the "warm" temperature. Turn off the car when done.

7) Repeat steps 1-6 with a different car. T_{hot} = _____ ^{o}C

8) **Be sure to write down the make and year of each car. There will be a competition for the cleanest/dirtiest car at the end!**

9) On the way back to lab and once away from the parking lot, use the last syringe to get a "background air" sample as a reference. Flush the syringe twice with air. Draw in 12.5 mL of indicator solution and then draw in air until 30 mL has been reached in the syringe. Cover the syringe with aluminum foil and shake the syringe vigorously for a few seconds. Lab the syringe as "background air". Take the temperature: T_{air} = _____ $^{o}C.$

IV: Analysis of the standards and exhaust samples

1) With the UV/VIS turned on, open the software program as shown in the instructions near the spectrophotometer or as shown by your TA. Perform a baseline correction with the indicator solution (solvent) in both cuvettes. Be sure to only touch the frosted sides of the cuvettes and always condition them 3-4 times with new solutions. Tap away any air bubbles before placing the cuvettes in the spectrophotometer and make sure the outside of the cuvettes are clean. Place the cuvettes with the frosted side facing you (allowing the beam of light to pass through the clear side of the cuvette).

2) Replace the indicator solution in the sample cuvette (closest to you) with one of the calibration standards, rinsing it our several times to condition it, and then measure the absorbance spectrum. Record the peak absorbance at 550 nm in the Data Table on the next page.

3) Repeat step 2 for the remaining calibration standards, the background air sample, and the exhaust samples in the syringes. Shake each sample before filling the cuvettes and make sure to condition the cuvette 3-4 times for each new sample.

Data Table: NO_2^- concentration vs. Peak Absorbance measured at 550 nm.

Sample	Absorbance

DATA ANALYSIS

1) From the mass of $NaNO_2$ provided on the stock solution flask, calculate the actual NO_2^- concentrations in μg/mL for each standard solution. Watch the dilutions!

2) Develop a Beer-Lambert Law plot (on the laptop computer provided) for the nitrite standards and perform a least squares analysis of the linear best fit line (Microsoft Excel instructions for graphing are in the Appendix if needed). This will give you a dependence in the form:

$$Absorbance = slope \times C + offset \qquad (y = mx + b)$$

3) Using the *slope* and *offset* parameters determined from your fit, calculate the concentration of nitrite (in μg/mL) in the cold and warm exhaust samples.

4) Use the equation below to convert the concentration of nitrite in the solutions to the concentration of NO_2 μg/L = ppm W (part per million by weight) in exhaust.

$$\frac{\mu g\ NO_2}{L} = \frac{\mu g\ NO_2^-}{mL}\left(\frac{1.39\ mol\ NO_2}{1\ mol\ NO_2^-}\right)\left(\frac{V_{in}}{V_{gas}}\right)\left(\frac{1000\ mL}{L}\right)$$

The stoichiometric factor 1.39 is empirical (it should be 2 according to equation 11), V_{in} is the volume of indicator solution in the syringe, and V_{gas} is the volume of exhaust gas in the syringe.

5) The concentration of NO_2 calculated in step 4 represents all the NO_x in the exhaust sample. To calculate the NO_x mixing ratio in ppmV (part per million by volume), use the following equation:

$$\text{ppm } NO_x = \ \mu L \ NO_x/L = \left(\frac{\mu g \ NO_x/L}{46.01 \ g/mol} \right) \left(\frac{RT}{P} \right)$$

where 46.01 g/mol is the molar mass of NO_2, R is the universal gas constant (0.08206 L atm/mol K), T is the Kelvin temperature at which the sample was collected, and P is the pressure.

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