Name: **GRACE KIM**

University of Pennsylvania
Chemistry 505
Environmental Chemistry

Summer 2008

Problem Set #4, Part 1. Using Excel statistics to verify a pressure/volume relationship (turn in this sheet and your Excel work).

Use the data below (from Table 5.1 in Zumdahl, *Chemical Prinicples* (5^{th} ed)). In this case, let X = pressure, **P**, (inches of Hg) and Y = volume, **V**, (in^3).

1. Convert inches of Hg to kPa to get **P** (best done using Excel).
   # inches x (2.54 cm/ 1 in) x (10 mm/ 1 cm) x (101.325 kPa/ 760 mm) = # kPa
   See excel spreadsheet.

2. Convert in^3 to liters to get **V**.
   # in^3 x (2.54 cm/ 1 in)^3 x (1 L / 1000 cm^3) = # L. See excel spreadsheet.

3. According to Boyle's Law, **PV** is constant when n, R and T are constant which implies a very high anticorrelation between **P** and **V**. Calculate and write below the correlation of P^{-1} and **V** using Microsoft Excel (consider using the regression program for this, which you'll use for question #4).
   The correlation r between P^{-1} and V is calculated to be 0.999901 (See attached Excel sheet).

4. Identify the slope using the regression program in Excel. (Turn in your regression result from Excel).
   The slope is 77.13170731 L kPa (see attached Excel sheet).

5. Manually calculate the slope of the regression line of P^{-1} and **V** (calculate a ratio of **ΔV to Δ P^{-1}**). How does this value differ from your Excel version?
   Slope = $\Delta y/\Delta x = (y_2-y_1)/(x_2-x_1)$ using the two points (0.006, 0.45) and (0.009, 0.7).
   = 83.3
   The value is pretty close to the calculated value, but probably not as accurate since the value of the points used to calculate the slope were just estimated by eye.

6. What is the significance value (ρ) calculated by Excel? Is this P^{-1},**V** relationship significant at the 95% confidence level? At 99%?
   The p-value for the slope is 1.17E-06. **The P^{-1}V relationship is significant at the 95% and 99% confidence level because 1.17E-06 < 0.05 (for the 95% confidence level) and <0.01 (for the 99% confidence level) and therefore the null (that there is no correlation between the two variables) can be rejected.**

7. Are you confident that there is a linear relationship between the P^{-1} and **V** variables? Why? **Yes, I am confident that there is a <u>linear</u> relationship between the two variables because the coefficient of correlation, r=** 0.999901428, **is almost 1, which means the strength of linear relationship between the two variables is very high.**

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8. Are there clear dependent and independent variables in this relationship? Why?
   No, there are no clear dependent and independent variables in this relationship. The relationship is strong, but you can manipulate either the pressure or the volume to affect the other variable.

Part 2: Some questions about stratospheric ozone.

According to Baird, there is a relationship between energy and wavelength of radiation that can be calculated using:

$E = hc / \lambda$

E = energy, kJ mol^{-1}
h = Planck's constant
c = speed of light
λ = wavelength, nm

When converted to get units of E= kJ mol^{-1} and λ = nm,

$E = 119627 / \lambda$

We know that the bond energy of C – Cl (from $CFCl_3$) is 338.9 kJ mol^{-1}. If one of these bonds is broken, $Cl^{\cdot}$ is released and can react with other things.

9. What is the longest wavelength of light is needed to break this bond (assuming that the molecule absorbs this wavelength).

$\lambda = 119627 / E = 119627 / 338.9$ kJ mol^{-1} = 353.0 nm (longest wavelength, minimum energy)

10. Is this wavelength found among light sources that we receive in the troposphere?

Yes, this wavelength light is found in the troposphere. This wavelength is UV-A (320-400 nm) and is not absorbed by the O_3 layer in the stratosphere.

11. Since $CFCl_3$ is considered stable in the troposphere, what does your answer to #10 tell you about the absorption of this wavelength by this molecule?

Because $CFCl_3$ is stable in the trophosphere, $CFCl_3$ does not absorb the wavelength.

12. $CFCl_3$ is dissociated by UV radiation in the stratosphere. What does this tell you about the wavelengths this molecule *does* absorb?

The wavelengths that $CFCl_3$ must absorb to break the C-Cl bond must be in the UV-B (320-280 nm) and UV-C (280-200 nm) range of wavelengths, which is present in the stratosphere, but is filtered out by ozone and not present in the troposphere.

13. The Cl-Cl bond energy is 243 kJ mol^{-1}. What is the longest wavelength of light that will dissociate Cl_2?

$\lambda = 119627 / E = 119627 / 243$ kJ mol^{-1} = 492 nm (longest wavelength, minimum energy)

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14. Where in the electromagnetic spectrum is the wavelength found that you calculated in #13? (That is, UV, visible, IR, TV/radio, etc).

492 nm is found in the visible range (400-700 nm)—blue, green light.

15. If volcanic eruptions of chlorine are in the form of Cl_2, what does your answer to #14 tell you about the longevity of this source of atmospheric chlorine? Why?

The Cl_2 from volcanic chlorine rapidly dissociates because there is lots of visible light in the troposphere. Therefore, this source of atmospheric chlorine does not have great longevity (it breaks down rapidly into atomic chlorine and does not persist as diatomic chlorine).

16. The dissociation of Cl_2 results in formation of chlorine radicals, $Cl^{\cdot}$ What *can* become of this radical in a polluted atmosphere containing NO_2?

The chlorine radical can react with ozone to make ClO•, which then reacts with NO_2 to form chlorine nitrate, $ClONO_2$, which is a catalytically inactive reservoir for the ClO radical. This $ClONO_2$ molecule can then over following hours or days photochemically decompose back into its components to re-yield the ClO• which can then continue to catalytically decompose ozone by Mechanism II.