University of Pennsylvania
Department of Chemistry
Chemistry 505 – Environmental Chemistry
Summer 2008

PIM #1a. Due July 7, 2008. Presentations on July 7.

Estimating the enthalpy of vaporization, ΔH_{vap}, of semivolatile industrial compounds, (polychlorinated biphenyls, or PCBs) using the Clausius-Clapeyron equation.

Synopsis: The enthalpy of vaporization, ΔH_{vap} is an important piece of information when investigating movement of semivolatile compounds into and out of the atmosphere. When these compounds are moved into the gas phase from a liquid, energy is applied in the form of insolation or simply warmer air. Once in the gas phase, these compounds move where the winds take them. When encountering cooler air, they may condense by losing the amount of energy that had been applied. In effect, ΔH_{vap} tells us how much energy must be applied to put the substance into the gas phase and how much must be taken away to make it condense.

For many industrial compounds and pesticides found in the environment, the value of ΔH_{vap} is not known. But it can be estimated from air concentration data by using the Clausius-Clapeyron equation:

$$\text{Ln } P = (-\Delta H_{vap} / RT) + c$$

where P = partial pressure of the gas (in atm or Pa) (y-axis)
R = gas constant (atm or Pa form)
T = temperature (x-axis)
c = constant (the y-intercept)

Note that this is a linear equation where T is the variable.

Historically the CC equation was used to measure vapor pressures of substances in a closed atmosphere where the temperature was varied. Technically it should be applied only to closed systems, but environmental chemists use it often to estimate ΔH_{vap} because there is nothing else that works.

Note that when ΔH_{vap} becomes the unknown the form of the equation changes to this:

$$- \Delta H_{vap} = RT \text{ Ln} P – c$$

Note also that Ln P will always be negative because the partial pressure is always < 1 atm. In that case, there are negative values on both sides of the equation and ΔH_{vap} becomes positive, indicating that the process is endothermic, which we know is true.

Environmental chemists generally agree that when ΔH_{vap} is a large positive value there is a local source of the contaminant of interest (COI) at the sampling site because there will be high local concentrations of the contaminant in summer and low concentrations in winter. When the value of ΔH_{vap} is very small, it is considered that local temperature changes are not influencing contaminant concentrations and that the contaminants are being transported from somewhere else. This is not always true for reasons that we will discuss in class.

For this PIM, your job will be to take real data collected some years ago in Michigan and apply the Clausius-Clapeyron equation to it to estimate ΔH_{vap} and then draw some conclusions about what the data are telling you. There are sampling data for four sites in Michigan, so there will be one site assigned to each of four PIM groups. The contaminants of interest (COI) to this study are in a class called polychlorinated biphenyls (PCBs). In this data set, about 120 different PCB congeners in 10 homologues were anayzed (although all 120 were never observed in any individual sample). Each person in each PIM group will be assigned one congener to work on. The set of congeners will be the same for each of the four groups. That way, we can have within group comparisons (how different congeners are showing different ΔH_{vap} values) and across groups comparisons to show how one congener is behaving at different sites where temperatures are different.

The value of ΔH_{vap} will be calculated from the Analysis toolpak in Microsoft Excel. You will also get regression statistics for these data telling us the correlation and the significance level of Snedecore's *F*.

The four sites (and name abbreviations) are:

South Haven, MI (SHA)
Dexter, MI (DEX)
Deckerville, MI (DKW)
Pellston, MI (PEL)

The data cover the period from May 1992 to the end of February 1994. Samples were collected on the same date every 6 days from these sites. Some dates are missing because not all of the samples were analyzed. The most complete sample set is for SHA.

The PCB congeners of interest to this study are:

PCB 18: 2,2',5-trichlorobiphenyl
PCB 33: 2',3,4-trichlorobiphenyl
PCB 56: 2,3,3',4, -tetrachlorobiphenyl (coelutes with PCB 60, 2,3,4,4'-tetrachlorobiphenyl)
PCB 138: 2,2'3,4,4',5 -hexachlorobiphenyl (coelutes with PCB 163, 2,3,3',4',5,8-hexachlorobipohenyl

The data are arranged in tables by Julian date (the date code 92-355 or 92355 for example refers to 1992, day 355, or December 22).

Data tables are posted on Blackboard.

You will need to take your assigned data, which are in ng m^3, and convert to pg m^3. Then convert the value of concentration to moles L^{-1} and then to partial pressure using the ideal gas law as indicated in Hermanson et al. (2007). Use the temperature given in the data set after conversion to K. Use either version of the gas constant but remember to keep your pressure units consistent. The conversion when pressure is stated in atm is:

$P = (C/MM)\ RT(10^{-15})$

Where C = concentration (pg m^{-3})
MM = molecular mass
R = gas constant
T = temperature (K)
P = partial pressure (atm or Pa)

Use the regression function in Excel's Analysis toolpak to calculate the regression constants (slope and intercept). The slope is equal to $\Delta H / R$. Then determine the value of ΔH by multiplying by the correct value of R. Remember that even thought the value of $\Delta H / R$ is negative (the slope is negative), the sign of ΔH is positive. Be certain to produce a graph from Excel of this relationship.

Within your group, compare all values of ΔH that have been calculated. Also, compare your value to that of the same congener from the other groups (that is, other sites).

Presentations: On Monday, July 7, you will assemble by groups (sites) and each individual will give a presentation on the results to the rest of the class. Each person will present results of the data analysis for not more than 5 minutes. Prepare a few Powerpoint slides (including your CC graph) that include the information you are giving the audience. Things to consider including in your presentation:

- Is your regression strong ($r > 0.7$)?
- Is the F statistic significant at the 95% confidence level (<0.05)?
- Can you determine how much energy is required to put your PCB congener into the gas phase at your site? If so, what is that value?
- Is there an indication that you have a local source of your congener at your site a high value for ΔH_{vap} (>50 kJ mol^{-1})?
- Look up the Henry's Law constant (HLC) for your compound at http://www.syrres.com/esc/physdemo.htm

Select a spokesperson to give a summary of the results for your site-based group. This person should be the last to give his/her individual presentation and then finish with the group summary. Things to consider:

- Which congeners have the highest and lowest ΔH_{vap}?
- Is there a consistent relationship between the ΔH_{vap} and HLC?
- Is there an indication that there is a local source of any of the congeners?

Turn in: Your Excel statistical data table for regression, your CC plot and a written summary of your conclusions. This should be very brief. This should be turned in electronically via e-mail or digital dropbox.

PIM 1b. Presentations on July 9.

Take the data that you calculated for PIM 1a and regroup by congener (that is, for example, all people analyzing PCB 18 should group together). Prepare a combined presentation considering the following:

- Which sites had strong and significant regression relationships between Ln P and T^{-1}? Which did not?
- Do results from any sites indicate that there is a local source of this particular PCB congener? Any that do not?
- What is the fraction of total PCB concentration contributed by this congener at the 4 sites (best way to do this is to average the fraction of total PCB for all samples at each site).
- Compare the average fraction of this congener in total PCB at each site with the fraction found in Aroclor 1242 (the most widely-manufactured PCB product in the USA). Use the data below for this. Do a *t*-test to determine if these averages are different from each other. Use the pooled-variance t-test in Excel as indicated on p. 149 of Levin and Stephan.

For the fourth bullet, use these ave and stdev and n values from Frame:

	Ave	Stdev	n
PCB 18:	8.53	0.602	3
PCB 33:	4.85	0.389	3
PCB 56:	1.80	0.098	3
PCB 138:	0.18	0.037	3