

## Generic Announcements

- Anyone needing to add, etc-see me after class
- Final exams for 221 can be picked up in my office
- Workshops
  - <http://web.pdx.edu/~wamserc/ChemWorkshops/299W04.htm>
- No breaks this quarter until we catch up-those of you who are in the habit of going for beer at 6:40pm can feel free to leave-my feelings won't be hurt
- The Tuesday afternoon group meetings will continue this quarter
- Chem 222 is considerably more challenging than 221

# Introductory Issues

- Web material for the course is found via <http://web.pdx.edu/~gwwiger>
- Syllabus has detailed description of course structure, etc. Basically the format will follow what was done in Che 221. Given the weather disruption, just move everything back by a week, initially( we will catch up eventually), **except for the exams-which will be held on the scheduled dates.**
- Students need to be aware that the course is cumulative beginning with Che 221. Key issues from 221 with which the student needs to be comfortable and which should be reviewed as needed:
  - General analysis of 3 variable systems, “changes of state” for binary systems
  - Mathematical skills will be critical in this course
  - All aspects of nomenclature
  - All aspects of dealing with chemical formulas
  - All aspects of stoichiometry
  - Solutions

# Thermodynamics/Thermochemistry

- “Changes of State” whether physical or chemical are usually accompanied by energy changes
- What is energy-a quick tour (don't tell the physics people)
  - Energy =>The ability to do work
    - can be either positional (potential) or due to motion(kinetic)
  - What is work => $F \cdot d$  (something moves)
  - Since  $F=ma$   $\text{kg} \cdot (\text{m}/\text{sec}^2)$
  - It follows  $E=(\text{kg} \cdot \text{m}^2)/\text{sec}^2$
  - This is called a Joule and is the SI unit of energy
  - More “real”-the calorie which is the amount of energy accompanying a one deg C change in temperature by one gram of liquid water. One calorie is exactly 4.184 J
  - You will find many energy values in calories and you must be able to work comfortably with both Joules and calories and interconvert them.

# Generic changes of state and some sign conventions

- A system is whatever the study defines/includes. Everything not part of the system is part of the surroundings
- Our interest is in the system undergoing changes of state  
State<sub>1</sub> => State<sub>2</sub> with an accompanying change in the internal energy  
 $\Delta E = E_2 - E_1$
- Some rules
  - If energy is lost  $\Delta E < 0$ . If gained  $\Delta E > 0$
  - The energy change can be heat (q), work (w) or both
  - $\Delta E = q + w$  (you'll also see  $\Delta E = q - w$  => sorry about that!)
  - All changes are viewed as the result of interaction of the system with the surroundings. Thus the signs of q and w, as well as the process descriptions, must be consistent with the signs of  $\Delta E$ .
    - Loss of heat=loss of energy( $q < 0$ ); gain of heat=gain in energy( $q > 0$ )
    - Work done by the system=loss of energy( $w < 0$ ); work done on the system=gain of energy( $w > 0$ ).
  - One often hears of the standard state. This is not that tightly defined due to variation in what the temperature is. It does require that the substance be in its most stable form at 1atm and the specified T and that all concentrations be 1M.

# A few details

Work by chemical systems usually takes the form of expansions/compressions resulting from changes in P and/or V.  $\Delta(PV)$  is a general way of describing this. Obviously, if both P and V change, the analysis can get quite complex, usually requiring the use of calculus. To simplify the system while still getting the point across, we restrict the changes to constant P conditions (more about that later). The work then becomes a function of  $P\Delta V$ . However, we don't want to make this too simple, do we?  $\Delta V = V_2 - V_1$ .

$\Delta V > 0$  ( $P\Delta V > 0$ ), the system expanded and did work on the surroundings, therefore  $w < 0$  (energy lost by the system)

$\Delta V < 0$  ( $P\Delta V < 0$ ), the system was compressed and work was done in it by the surroundings, therefore  $w > 0$  (energy gained by the system)

Conclusion:  $w = -P\Delta V$ . note:  $1.00\text{L}\cdot\text{atm} = 101\text{J}$

Signs of  $\Delta E$

- $q < 0$  &  $w < 0$   $\Delta E < 0$
- $q > 0$  &  $w > 0$   $\Delta E > 0$
- $q < 0$  &  $w > 0$   $\Delta E < 0$  or  $\Delta E > 0$
- $q > 0$  &  $w < 0$   $\Delta E < 0$  or  $\Delta E > 0$

# A quick look at phraseology

- $\Delta E = q + w$                        $30 = 40 - 10$
- 1. What is the change in internal energy if a system gains 40J in heat while performing 10J of work?
- 2. A system does 10J of work on the surroundings while gaining 40J of heat. What is  $\Delta E$ ?
- 3. The performance by the system of 10J of work is accompanied its gaining 40J of heat. What is  $\Delta E$ ?
- 4. If the internal energy increases by 30J when the system gains 40J of heat, what is  $w$ ?
- 5. The heat content of the system increases by 40J and its internal energy also increases by 30J. What is  $w$ ?
- 6. If 10J of work is done on the surroundings while the internal energy increases by 30J, what is  $q$ ?
- 7. The system has an internal energy increase of 30J while gaining 40J of heat, what will the work be?
- 8. It is found that  $\Delta E = 30J$  upon the performance of 10J of work by the system. What is  $q$ ?

# The real world-specific heat and heat capacity

- *Specific heat*- the amount of heat accompanying a one degree C temp change of one gram of a pure, homogeneous substance-the symbol  $C_s$  will be used to represent specific heat which has the units of J/(g-deg) or cal/(j-deg)
  - $q=C_s*m*\Delta T$  ( $\Delta T =T_2-T_1$ )
- *Heat capacity*-the amount of heat accompanying a one deg C temp change of any defined entity. The symbol  $C_p$  will be used to represent heat capacity which has the units J/deg or cal/deg
  - $q=C_p*\Delta T$
- You will also encounter the quantity *molar heat capacity*( $C_n$ ) (self explanatory) J/(mole-deg)
  - $q=C_n*n*\Delta T$
  - It is of interest that there is much less variation between molar heat capacities and specific heats. In fact, for metals molar heat capacities are nearly all the same( $\sim 25$ J/mole). Why?

# Heat transfer

- Energy will flow between two “objects” at different temperatures until temperature equilibrium has been attained. Why?
- The first law of thermodynamics requires that
$$q_{\text{lost}} + q_{\text{gained}} = 0 \text{ or } |\text{heat lost}| = |\text{heat gained}|$$
- The actual analysis of such systems can be fairly complex. For example, if two samples initially at different temperatures are mixed, the result is described by the equation:

$$(C_s * m * (T_2 - T_1))_{\text{sample 1}} = - (C_s * m * (T_2 - T_1))_{\text{sample 2}}$$

A key point is to remember that the  $T_2$ s are the same. This still leaves us with 7 variables. So much for the three variable system.



# Enthalpy

- $\Delta E = q + w$
- $w$  is normally described as the work of expansion. In other words, the volume changes. This is  $\Delta(PV)$  work.
- $\Delta(PV)$  can be looked at in many different ways, but it is sufficient, for our purposes to consider two very limited cases.
  - Constant volume systems-no expansion is possible,  $\Delta(PV) = 0$ ,  $w = 0$ ,  $\Delta E = q_v$
  - Constant pressure (open container changes)  $w = -P\Delta V$ . In such cases we define a new quantity enthalpy,  $\Delta H = q_p = \Delta E + P\Delta V$ .

# State functions and the 1<sup>st</sup> Law

- The first law of thermodynamics states that the energy of the universe is constant. This also requires that the energy of any fully defined state of a system be fixed and constant. Why?
- Any process which starts and ends at the same position, energetically, must therefore have a  $\Delta E=0$ . This does not restrict, a priori, the values of  $q$  and  $w$ . In principle, there exists an infinite number of combinations of  $q$  and  $w$  for any specific value of  $\Delta E$ . A cyclic process for which  $\Delta E$  was not equal to zero would change the energy of the universe.
- Any function which depends only on the starting and ending points for a change of state is termed a state (or path independent) function.
- Enthalpy is a state function.
- The vast majority of thermodynamic values you encounter are enthalpies.

# Hess' Law

- *Recherches thermochimiques*

- *Germain Henri Hess*

- *Bulletin scientifique*

- Académie impériale des sciences*

- Volume 8, p. 257-272*

- St. Petersburg, 1840*

- *A combination having taken place, the quantity of heat evolved is always constant whether the combination is performed directly or whether it takes place indirectly and in different steps.*

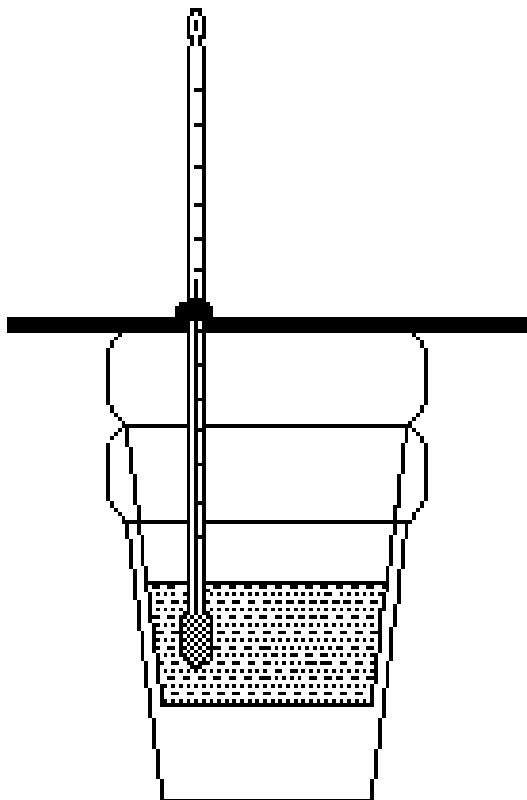
## Some specific enthalpies(a sampling)

- **Heats of fusion**, vaporization, sublimation, etc. per mole of species.
- **Heats of formation**: enthalpy accompanying the formation of one mole of a chemical compound from its component elements. Heats of formation are negative for stable compounds(relative to their elements) and 0 for elements in their “normal” form.
- **Bond energies**-energy required to homogeneously **break** a bond(per mole)-always positive
- **Heat of combustion** (normally for hydrocarbons:compounds containing only C and H)-enthalpy of reaction of the compound (one mole)with oxygen yielding CO<sub>2</sub> and water. highly negative.

# Experimental Thermochemistry-Calorimetry

- The actual measurement of heat changes is done via calorimetry which simply measures changes in temperature for a system insulated sufficiently from the surroundings such that the “leakage” is insignificant in the measurement timeframe.
- Such a process most often involves the measurement of changes in temperature of a reservoir of water. The only “special term” is the heat capacity of the device-often termed the calorimeter constant. By measuring the change in temperature of the calorimeter and its contents, it is possible to calculate the heat change for the process under study.
- Depending on whether it is an open or closed calorimeter, either  $q_v$  or  $q_p$  is determined.
- The general equation looks something like:
  - $q = (C_{p(\text{calorimeter})} + 4.184 \cdot m_{\text{water}}) \cdot \Delta T$
  - In most cases there will be additional terms dependent on the exact nature of the experiment

# Coffee Cup Calorimeter



# A bomb calorimeter



# Stoichiometry of heat-Thermochemical Eqns

- When an enthalpy is attached to a balanced chemical equation-it becomes a thermochemical equation.
  - $\text{CH}_4(\text{g}) + 2\text{O}_2 \Rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$
  - $\text{CH}_4(\text{g}) + 2\text{O}_2 \Rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad \Delta\text{H} = -890\text{KJ}$
- The enthalpy can/must be treated stoichiometrically just like any of the chemical species in the reaction. Why?
- Thus, you talk about the stoichiometry of heat.
- Basic rules:
  - multiply the reaction-multiply the enthalpy by the same term
  - reverse the reaction- change the sign of the enthalpy



# Using Hess' Law

- Born-Haber Cycles-you should remember these from 221
- Combining chemical reactions(generic)
  - $A+2B \Rightarrow C \quad \Delta H=10J$
  - $C+D \Rightarrow A + F \quad \Delta H=20J$
  - therefore:  $D + 2B \Rightarrow F \quad \Delta H=30J$
  - more about this later
- Using Heats of Formation
  - $C_2H_4(g) + 3O_2(g) \Rightarrow 2CO_2(g) + 2H_2O(l)$
  - could be described as resulting from the following:
    - $C_2H_4(g) \Rightarrow 2C(s) + 2H_2(g) \quad - \Delta H_f(C_2H_4)$
    - $2C(s) + 2O_2(g) \Rightarrow 2CO_2(g) \quad 2*\Delta H_f(CO_2)$
    - $2H_2(g) + O_2(g) \Rightarrow 2H_2O(l) \quad 2*\Delta H_f(H_2O)$
    - Since the above three reactions sum to the overall reaction, the enthalpy is the sum of those shown  $\Delta H_{rxn}=2*\Delta H_f(CO_2) + 2*\Delta H_f(H_2O) - \Delta H_f(C_2H_4)$
    - more generally

$$\Delta H = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$$

- Using Bond energies
- Many chemical reactions can be described in terms of bond breaking and formation
  - $\text{H}_2 + \text{Cl}_2 \Rightarrow 2\text{HCl}$  could be viewed as the breaking of H-H and Cl-Cl bonds followed by the forming of 2 H-Cl bonds. This lets one state  $\Delta H = (\text{BE}_{\text{H-H}} + \text{BE}_{\text{Cl-Cl}}) - 2 * \text{BE}_{\text{H-Cl}}$
  - more generally  $\Delta H = \sum \text{Bonds broken} - \sum \text{bonds formed}$
  - application of this requires a detailed understanding of the reaction process
- Why reactions occur-the enthalpy view. If one takes the simple view (too simple actually) that reactions with negative enthalpies (give off heat) are favorable, the above two applications of Hess' Law can give a sense of why processes occur:
  - The products are more stable than the reagents
  - the bonds formed are stronger than those broken.

# Bring on the Problems

- A few introductory cautions:
  - As with many computations in chemistry, there is nothing intrinsically complex about the mathematics(easy for me to say). It's all about the details
  - Signs are critical
  - Pay very close attention to details:
    - which temp is  $T_1$
    - Is it  $C_s$  or  $C_n$
  - Always form some kind of expectation
  - Watch the actual math
- System absorbs 34.5J of heat while performing 62.3J of work. What is  $\Delta E$ ?
  - $\Delta E = q + w = 34.5 - 62.3 = -27.8\text{J}$
- What is the heat change if 24.5g of water go from  $18.5^\circ$  to  $67.3^\circ$ ?
  - $q = C_s * m * \Delta T = 4.184 * 24.5 * (67.3 - 18.5) = 5000\text{J} = 5.00\text{KJ}$

- A horseshoe at a temperature of 640°C with a heat capacity of 478J/deg is dropped in to 5.00L of water at 25°C. According to a strict thermodynamic treatment-what happens? What would you actually observe?

- $q_l = -q_g \quad (C_p \cdot \Delta T)_{\text{horseshoe}} = -(C_s \cdot m \cdot \Delta T)_{\text{water}}$

- $478 \cdot (T_2 - 640) = -4.184 \cdot 5000 \cdot (T_2 - 25)$

- solving yields  $T_2 = 38.7^\circ$

- checking

- $478 \cdot (38.7 - 640) = -28700$

- $4.184 \cdot 5000 \cdot (38.7 - 25) = 28700$

- The heat of combustion of a methane is -890KJ/mole.

- What is it in KJ/g?

- $(890\text{KJ/mole}) \cdot (1\text{mole}/16\text{g}) = -55.6\text{KJ/g}$

- How many grams are needed to heat a cup of water (100.mL) from 20.0° to 95.0°C so you can make some tea? Why is this number not correct?

- $q_{\text{water}} = C_s \cdot m \cdot \Delta T = 4.184 \cdot 100\text{g} \cdot 75^\circ = 31380\text{J} = 31.4\text{KJ}$

- $31.4\text{KJ} / (55.6\text{KJ/g}) = .565\text{g}$