Announcements – 10/16/00

- ***<u>Exam #2:</u>*** Wednesday, 10/18, 7:00 pm
  - *A141 Cook*
  - *<u>Exam #2 Info Page</u>*

- ***<u>Demo Today!</u>***

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First Law of Thermodynamics

- "The total energy of the universe is *constant*."
- "Energy is neither created or destroyed in a process, only converted to another form."

  -**Conservation of Energy**
- "*You can't win . . . you can only break even.*"

$$\Delta E = q + w$$

Change in energy of the system (ΔE)

Heat Flow (q):
+ is **<u>into</u> system**
- is <u>out of</u> system

<u>Work:</u> + is done **<u>on</u> system**
- is done **<u>by</u> system**

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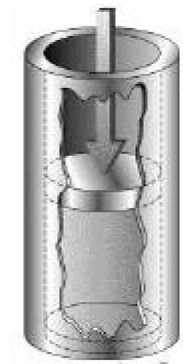
Example: Gas in a cylinder (fixed volume)

- Suppose we have a gas in a cylinder with a movable piston:

•<u>What if:</u>



•The piston is locked in a fixed position

-Volume is *constant*, so: **<u>w = 0</u>**

-> w = f x d OR <u>$w = P\Delta V = 0$</u>

<u>Thus</u>: $\mathbf{\Delta E = q_v}$

•Now, if we add *heat* to the system:

q > 0, so <u>$\Delta E > 0$</u> (E incr.)

-temp incr -> $E_k = 3/2\ RT$ -> **<u>$\Delta E_k = 3/2\ R\Delta T$</u>**

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Example: Gas in a cylinder (variable volume)

- Ok, now let's allow the piston to move, but let's ***disallow heat flow*** (q = 0) - <u>*adiabatic process*</u>

<u>So:</u> $\Delta E = w = -P\Delta V$

Movie!

- <u>Gas Compression</u>: $\Delta V < 0$ -> <u>*D**E is +***</u>
  - -work is done *on* the system
  - -temperature of the gas *increases*
- <u>Gas Expansion:</u> $\Delta V > 0$ -> <u>*D**E is -***</u>
  - -work is done *by* the system
  - -temperature of the gas *decreases*

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Measuring ΔE

- We can measure ***q*** by the change in temperature:

  If **q > 0:** heat is *added* to the system
  -***endothermic*** (system absorbs heat)
  -temperature (*of the surroundings*) *<u>decreases</u>*

  If **q < 0:** heat is *given off* by the system
  -***exothermic*** (system loses heat)
  -temperature (*of the surroundings)* *<u>increases</u>*

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Calorimetry: Measuring ΔE

- We can quantify heat flow (q) by measuring the change in temperature of a system: *Calorimetry*

  <u>Heat Capacity (C)</u>: amount of heat (q) required to raise the temperature of a substance by 1 K

  -if we calculate C for a *specific amount* of a particular substance, we call it the ***Molar Heat Capacity*** *(c_v at constant volume)* or the ***Specific Heat Capacity*** *(c_s, per gram of the substance)*

<u>Example:</u> for 100.0 g H_2O -> *specific heat = 4.184 J/g - K*

C = mass x specific heat = m x c_s
= 100.0 g x 4.184 J/g - K
= ***<u>418.4 J/K</u>***

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Heat flow and temperature

- Now we can relate ***q*** and temperature:

$$q = C\,(T_{final} - T_{initial})$$

<u>Example:</u> How much heat is required to raise the temperature of *232.0 g* H_2O from **25.0 °C** to **78.0 °C**?

$q = C\Delta T = (m \times \text{specific heat})(\Delta T)$

$= (232.0 \text{ g} \times 4.184 \text{ J/g-K})(78.0 - 25.0)$

$= (970.688 \text{ J/K})(53.0 \text{ K})$

$= 51446.464 \text{ J} = \boldsymbol{5.14 \times 10^4 \text{ J}}$

= ***<u>51.4 kJ</u>***

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Constant-Volume Calorimetry

- Use a "bomb" calorimeter:

-typically used with *combustion* reactions

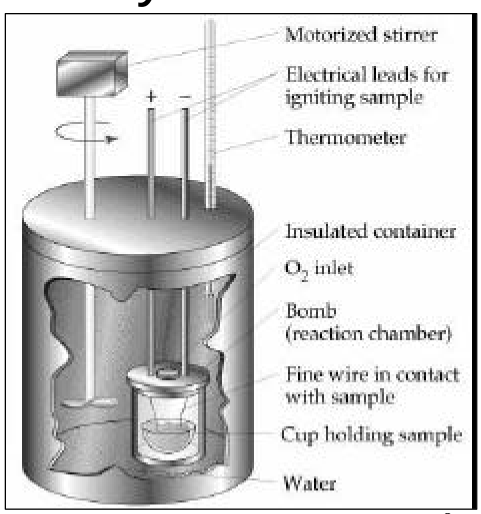
-heat (q) from rxn is transferred to the water and the calorimeter

-knowing the *heat capacity* of the calorimeter:

$q_{rxn} = -C_{cal} \times \Delta T$

<u>So:</u> $q_v = \Delta E$

(w=0 @ constant volume)



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Enthalpy

- Chemistry is commonly performed at *constant pressure*, so:
  - -it is easy to measure *heat flow* (q_p)
  - -work ($P\Delta V$) is small (but finite) and hard to measure

Define a new term: **Enthalpy (H)**

$$H = E + PV$$

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Relating Enthalpy and Heat

- Recall: $\Delta E = q + w$
- At constant pressure: $\Delta E = q_p - P\Delta V$
- Rearranging: $q_p = \Delta E + \Delta PV$

$$q_p = D(E + PV)$$

- Substituting: $q_p = DH$

So, if we measure q_p, then we can obtain the enthalpy change (ΔH) directly

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Constant-Pressure Calorimetry

- So-called "coffee-cup" calorimetry:

•Add reactants to cup

•Measure resulting temperature increase (or decrease)

•$q_{soln} = -q_{rxn}$

•<u>So</u>: $\Delta H = -q_{soln} = -m_{soln}(\text{sp heat})\Delta T$

•You will do this *this* week in lab!

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