February 4, 2002

- **Questions for Problem Session?**
- Exam #1
  - Wednesday, 2/13, 7 pm
  - *Conflict?* Email me this week
- **Day/time for Exam Review Session?**
- *Quiz post mortem*

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Thermodynamics

Chem 36

Spring 2002

Thermodynamics

- The study of *energy changes* which accompany physical and chemical processes

  Why do we care?

  -will a reaction proceed spontaneously?

  -if so, to what extent?

  It **won't** tell us:

  -how *fast* the reaction will occur

  -the *mechanism* by which the reaction will occur

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What is Energy? (review!)

- Energy is the ***capacity to do work or to transfer heat***

  -Kinetic Energy: energy associated with mass in motion (recall: $E_k = \frac{1}{2}mv^2$)

  -**Potential Energy:** energy associated with the *position* of an object relative to other objects (energy that is *stored* - can be converted to kinetic energy)

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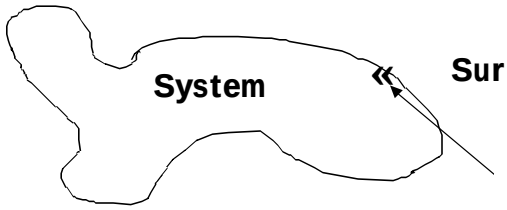
The System *(review)*

- We must define what we are studying:



System: portion of the universe under study

Surroundings: everything else

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First Law of Thermodynamics *(review)*

- "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 (state function)

Heat Flow:
+ is **into system**
- is out of system
(path function)

Work: + is done **on system**
- is done **by system**
(path function)

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Enthalpy *(review)*

- 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 *(review)*

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

  $q_p = \Delta(E + PV)$

- Substituting: $q_p = \Delta H$

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

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How are ΔE and ΔH related? *(review)*

- From the definition of Enthalpy:

$$\Delta H = \Delta E + P\Delta V$$

- for an ideal gas: $P\Delta V = RT\Delta n$

So: $\Delta H = \Delta E + RT\Delta n$

q_p q_v PV work

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ΔH and *Spontaneity*

- Shouldn't ΔH be a good indicator of reaction *spontaneity*?
  - ✓ If $\Delta H < 0$, products at a *lower energy* than reactants

Examples:

$CH_4\ (g) + 2O_2\ (g) \rightarrow CO_2\ (g) + 2H_2O\ (g)$ $\Delta H = -802$ kJ

$4Fe\ (s) + 3O_2\ (g) \rightarrow 2Fe_2O_3\ (s)$ $\Delta H = -1648$ kJ

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But what about . . .

These are spontaneous processes too:

$NaCl\ (s) \rightarrow Na^{+}\ (aq) + Cl^{-}\ (aq)$ $\quad \Delta H = +$

$H_2O\ (s) \rightarrow H_2O\ (l)$ $\quad \Delta H = +$

- Both are *nearly* enthalpy neutral
- Both result in *increased disorder*
- We need another LAW of thermodynamics!

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The 2nd Law of Thermodynamics

- "Spontaneous processes are accompanied by an *increase* in Entropy."
- "The Entropy of ***the Universe*** is constantly *increasing."*

So, what *is Entropy*?

- **Entropy** (S): A measure of the degree of disorder or randomness of a system
- Processes will tend towards conditions with the *highest probability* of occuring

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