Chemical Energetics

CHEM 107
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Reading, etc.

- Class: Chemical Energetics
  Reading: Chapter 9 (today & next week)
Reaction Energy

Reactants → Products

Reaction Energy: Energy taken in or given off during reaction

$$\Delta E = E_{\text{products}} - E_{\text{reactants}}$$

■ This is a conservation of energy statement.

Reaction Energy

■ If $\Delta E_{\text{reaction}}$ is negative, energy is given off.
  – “Exothermic”
■ If $\Delta E_{\text{reaction}}$ is positive, energy is absorbed.
  – “Endothermic”
■ We can NOT predict whether a reaction will occur based only on $\Delta E$!
**“Path Independence”**

\[ \Delta E = E_{\text{products}} - E_{\text{reactants}} \]

- This does not specify what might exist between reactants and products.

- \( \Delta E \) is “path independent.” We can imagine any set of steps that get us from the reactants to the products.

- Because changes in \( E \) are path independent, we say \( E \) is a “state function.”
Bond Energies and Reactions

- We can measure the strength and length of chemical bonds. (some easily, some with great difficulty)
- Energy of a particular type of bond (carbon - hydrogen, etc.) approximately (but not exactly) the same in different molecules.
- This is because bonds are often mainly localized and because orbitals used to make bonds are similar in different molecules.

Using Bond Energies: Reaction Energy

- Average bond energies are tabulated. (Table on the next slide is a short list.)
- We can use a full table of these to estimate the energy change for any chemical reaction.
- Decide whether the reaction was likely to succeed, evaluate possible fuels, etc.
Some Bond Energies (kJ/mol)

■ Diatomic molecules (actual values)
  H—H 436  O=O 494
  C≡O 1071  N≡N 942

■ Other bonds (avg. values)
  C—C 346  C≡C 602  C≡C 835
  C—H 415  C≡N 615  C≡N 890
  C—F 485  N=O 605
  N—H 390
  O—H 460
  O—F 190

Using Bond Energies

■ Imagine running the reaction as follows:
  – break every bond in reactants, giving a collection of atoms
  – make new bonds among these atoms to form products
  These ideas were introduced in Lecture 8.1

  Reactants → free atoms → products

■ Will each step cost energy, or release energy?
Using Bond Energies

- Can use bond energies to find the energy required or released in these imaginary steps. Get $\Delta E$ by combining these.

$$\Delta E_{\text{reaction}} = \sum \text{BE}_{\text{reactants}} - \sum \text{BE}_{\text{products}}$$

("\(\sum\)" means "summation")

**NOTE:** Because bond energies are defined relative to ATOM energies, this has a "reactants" minus "products" - not usual!

Acrylonitrile Synthesis

$$2 \text{C}_3\text{H}_6 + 2 \text{NH}_3 + 3 \text{O}_2 \rightarrow 6 \text{H}_2\text{O} + 2 \text{H}_2\text{C=CH–C≡N}$$

- Use bond energies to estimate $\Delta E$ for this reaction. Some data are on next slide.
Some Bond Energies (kJ/mol)

- Diatomic molecules (actual values)
  - H—H: 436
  - O=O: 494
  - C≡O: 1071
  - N≡N: 942

- Other bonds (avg. values)
  - C—C: 346
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Thermodynamics & Chemistry

- Study of the energy changes associated with chemical or physical processes.
- Chemical applications of principles you will study in physics & engineering
  - reaction energy, fuels, etc.
- Goal - to be able to predict whether or not a given reaction can occur, using simple tabulated data.
Thermodynamics vs. Kinetics

- Thermodynamics tells us things about the eventual outcome of a chemical reaction, but NOT about how fast the reaction might be.
- To know if something will happen fast, we need to consider kinetics.
- Need both thermodynamics and kinetics to assess practical usefulness of a reaction.

Thermodynamics: First Law & Calorimetry
Definitions, etc.

- Chapter 9 (Secs. 9.2 and 9.3) deals with a lot of terms: forms of energy, heat, work, system, surroundings, universe, etc.
- These will be discussed only briefly in class since there is little point in my reading definitions that you can read for yourself. You will be expected to know all this material.

Quick Definitions

- **Universe** = System + Surroundings
- **System** = That part of the universe we wish to study; **Surroundings** = everything else
- **Open System**: Exchanges both matter and energy with surroundings (often ‘real world’)
- **Closed System**: Exchanges energy, but not matter, with surroundings (idealized)
- **Isolated System**: no exchange of matter or energy with surroundings (idealized)
Changes of state & state functions

- In thermodynamics, we usually talk about some change in a system. The change in a property \( X \) is just

\[ \Delta X = X_{\text{final}} - X_{\text{initial}} \]

- \( X \) is called a state function if the value of \( \Delta X \) depends only on the initial and final states, & not on the path taken between them.

State Functions

- Common state functions include \( P, V, T, n_i, \ldots \)
- Equations of State: show the mathematical relationships between state variables (e.g., \( PV = nRT \) approximates real gases).
- Most books, including ours, use the convention that state functions are represented as capital letters. Lower case letters are usually not used for state functions.
Path Independence of State Functions

\[ \Delta X = X_{\text{final}} - X_{\text{initial}} \]

- This does not specify what might happen between initial and final states.
- \( \Delta X \) is “path independent.” We can imagine any process from initial to final states.

Energy, Heat, Work, ...

- Definitions not always same as in ordinary use
- Distinctions between these important
- Our discussion will be limited - you will get a more careful treatment in more advanced courses
Energy (E)

- Often defined as “the ability to do work.”
- Lots of different forms of energy, as we have seen: potential, kinetic, light, etc.
- We’ll emphasize chemical energy, which is the energy stored in the chemical bonds in a substance or released when such bonds are formed. Chemical energy can be converted into other forms of energy.

Internal Energy

- We often discuss the change in “internal energy” (or just the change in energy) of a system.
- Our chemistry book uses $\Delta E$ for this.
- We rarely talk about $E$ itself, because there is no absolute scale for energies.
- Physics books often use $\Delta U$ for the change in internal energy.
Heat (q)

■ “A transfer of thermal energy into or out of a system.”

■ Note that heat and temperature are not the same thing. Temperature is a measure of thermal energy, while heat is a change in thermal energy. Heat always “flows” from regions of higher T to those with lower T.

■ Also note that heat does not always produce a change in T....

Heat capacity: relating q & T

■ If we change T at constant P: \( q = nC_p\Delta T \)

■ n is number of moles of the substance

■ \( \Delta T \) is change in temperature

■ \( C_p \) is “molar heat capacity” of the substance

■ Also often see \( q = mc\Delta T \), especially in physics & engineering books. Here c is called “specific heat.” Just different units!
Work

- Thermodynamic definition: “energy transfer accomplished by a force moving an object some distance.”
- Work = force × distance; \( w = F \times d \)
- If nothing moves, no work is done!

\[
F \times d = (\text{mass} \times a) \times d \\
= \text{kg} \times (\text{m/s}^2) \times \text{m} \\
= \text{kg} \times (\text{m}^2/\text{s}^2) \\
\sim \text{mass} \times v^2 \sim \text{K.E.}
\]

Work in chemical reactions?

- Often, the only form of work which is done in a chemical process is “PV-work,” or “work of expansion or compression.”
- This is given by
  \[
  w = - P_{\text{ex}} \Delta V \quad \text{(note the sign)}
  \]
  when \( P_{\text{ex}} \), the external pressure, is constant.
- If \( P_{\text{ex}} \) varies as the process occurs, we need calculus to find that \( w \) is the integral of \(- P_{\text{ex}} dV\)
**PV-work**

**Units Check**

Pressure ~ Force/Area  
Volume ~ Area × Distance  
PV ~ Force × Distance  
~ Energy (or Work)

Work is done on system  
\[ w = -P_{\text{ext}} \Delta V > 0 \]  
because  
\[ V_{\text{final}} < V_{\text{initial}} \]

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**Example**

- An automobile piston with a radius of 5.0 cm is displaced by 8.0 cm after firing. How much work is done (on the system) in each firing stroke if the external pressure is 3.5 atm?
Set up the problem!

- Get necessary info:
  \[ \Delta V = \pi r^2 \cdot d \]
  \[ = \pi (5.0)^2 \cdot 8 \text{ cm}^3 \]
  \[ = 628.3 \text{ cm}^3 \]
  \[ = 0.6283 \text{ L} \]

Signs of \( q \) & \( w \)

- \( w > 0 \) when work is DONE ON the system
- \( q > 0 \) when heat is ADDED TO the system

Following these sign conventions consistently is often a major obstacle in treating thermodynamic problems! These are scientist’s definitions, engineers often change the sign of \( w \). (When that definition is used, then \( \Delta E= q – w \). We will never use that definition.)