ABE 201
Biological Thermodynamics 1

Module 15

Enthalpies of Reaction

(Combining Chemical Reactions with 1st Law Energy Balances)

Outline

- Enthalpy changes as a result of <u>chemical reactions</u> (including biochemical reactions)
- Review of Hess's Law
- Using Hess's Law and standard heat (enthalpy) of formation to calculate enthalpies of reaction
- Heats of combustion and tabulated enthalpies of reaction

Heats of Reaction

- Definition: Enthalpy change where stoichiometic quantities of reactants react completely in a single reaction to form products at same T & P
- Heat of Reaction ≡ $\Delta\hat{H}_r$ (T,P)
- Dependent upon temperature and pressure
- At low pressures (near 1atm), ideal gas law is true, thus $\Delta\hat{H}_r$ (T) and P can be ignored

Exothermic and Endothermic

1st Law Balance $\Delta\hat{H}_r\,(T,P) = Q$

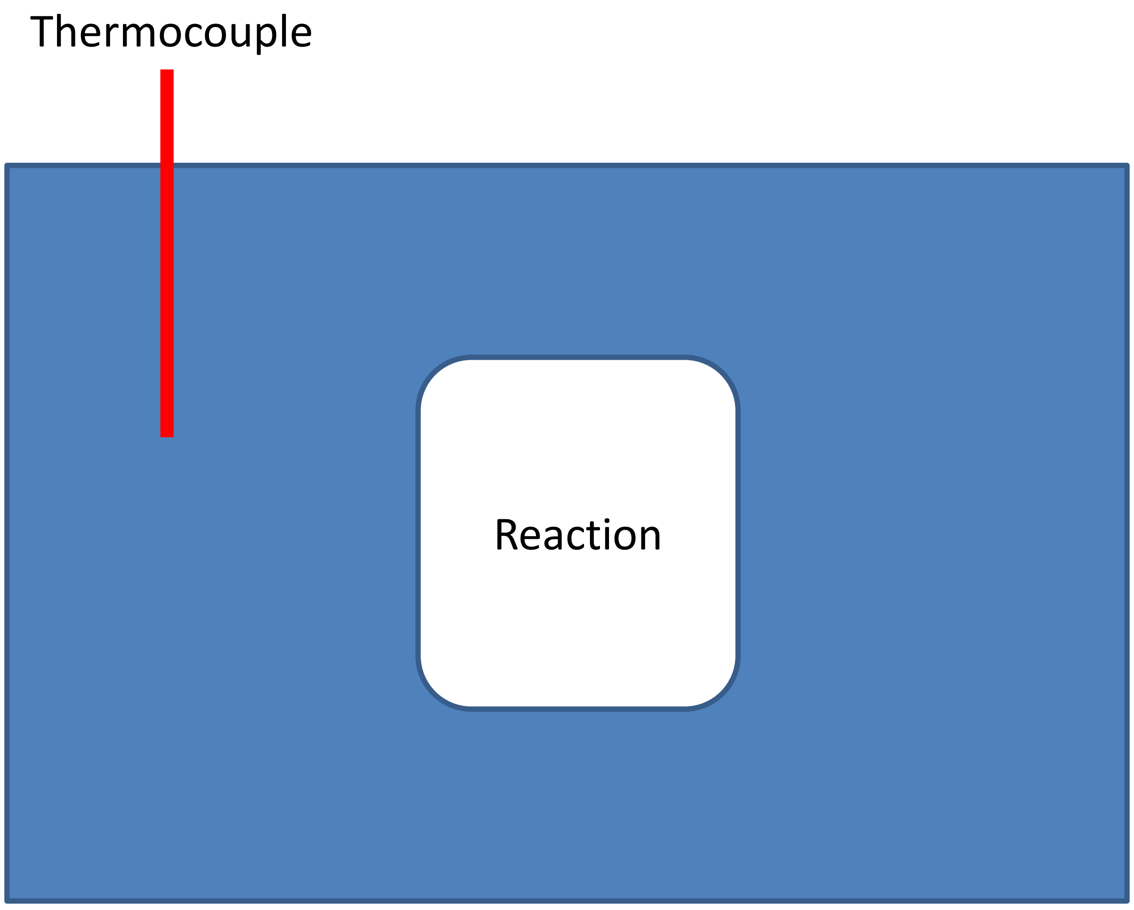
$\Delta\hat{H}_r\,(T,P) < 0,\ Q < 0$ Heat must be <u>removed</u>, to maintain constant T: <u>Exothermic</u>

$\Delta\hat{H}_r\,(T,P) > 0,\ Q > 0$ Heat must be <u>added</u>, to maintain constant T: <u>Endothermic</u>

Heats of Reaction

- Heats of Reaction may be measured directly
  - Calorimetry
- Heats of Reaction may be calculated
  - Hess’s Law

Calorimetry



Hess's Law

- If 1 reaction can be obtained by algebraic operations (+, -, x, ÷) of two or more reactions, $\Delta \hat{H}_r$ for reaction 1 can be obtained through the <u>same</u> algebraic operations on the $\Delta \hat{H}_r$ for the two or more reactions.

Hess’s Law - Example

$$2A + B \rightarrow 2C, \ \Delta\hat{H}_r = \text{-}1000 \text{ kJ/mol}$$

$$A + D \rightarrow C + 3E, \quad \Delta\hat{H}_r = \text{-}2000 \text{ kJ/mol}$$

$$B + 6E \rightarrow 2D, \qquad \Delta\hat{H}_r = ???$$

Solution

-2x (A + D -> C + 3E) = 2C +6E -> 2A + 2D

Add the above with the 1st eq:

  2A + B -> 2C

+ 2C +6E -> 2A + 2D

 2A + B + 2C + 6E -> 2A + 2C + 2D   (cancel out A and C)

B + 6E -> 2D

Algebraic operations: (eq 1) – 2*(eq2)

dHr = dHr1 – 2*dHr2 = -1000 + 4000 = 3000 kJ/mol

Heats of Formation

- Standard Heat of Formation ≡ $\Delta\hat{H}^\circ_f$ (T,P) ≡ The heat of reaction (enthalpy) to form a compound from its <u>elemental constituents</u>
- By definition, elements (as found in nature) have a $\Delta\hat{H}_f = 0$
  - As found in nature: O_2, N_2, H_2, C, Fe, etc.
- Standard Heats of Formation $\Delta\hat{H}^\circ_f$ (25 C, 1atm) are tabulated in back of text (table B.1)

Using Standard Heats of Formation

What is the heat of reaction for the combustion of ethanol (assume all reactants and products are gaseous)?

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O, \qquad \Delta\hat{H}_r = ???$$

Solution

Ethanol (g):
$2C + 3H_2 + ½ O_2 \rightarrow C_2H_5OH$, dHr = -235.31 kJ/mol

Oxygen (g):
O_2, dHr = 0 (by definition)

Carbon Dioxide (g):
$C + O_2 - > CO_2$, dHr = - -393.5 kJ/mol

Water (g):
$H_2 + ½ O_2 \rightarrow H_2O$, dHr = -241.83 kJ/mol

Algebraic Operations to Get to Desired Equation:

-1x Ethanol = $C_2H_5OH \rightarrow 2C + 3H_2 + ½ O_2$
2x Carbon Dioxide = $2C + 2O_2 \rightarrow 2CO_2$
3x Water = $3H_2 + 3/2\ O_2 \rightarrow 3H_2O$

Add them together:
$C_2H_5OH + 2C + 2O_2 + 3H_2 + 3/2\ O_2 \rightarrow 2C + 3H_2 + ½ O_2 + 2CO_2 + 3H_2O$
$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H20$

Heat of Reaction:
dHr = -1(etoh) + 2(co2) + 3(h2o) = -(-235.31) + 2(-393.5) + 3(-241.83) = -1277.18 kJ/mol

Standard Heats of Combustion

- Standard Heat of Combustion ≡ $\Delta\hat{H}^{\circ}_{c}$ (T,P) ≡ The heat of reaction (enthalpy) to combust (oxidize) a compound with oxygen
- Standard Heats of Combustion

  $\Delta\hat{H}^{\circ}_{c}$ (25 C, 1atm) are tabulated in back of text (table B.1)

  – Note that standard states of the products are all <u>gaseous</u> except <u>water</u>, which is liquid. To calculate with gaseous water as a product, add $44.01n_w$ kJ/mol where n_w is the number of moles of water formed

Standard Heat of Combustion

What is the heat of combustions for ethanol?

How does it compare to our calculate value?

dHc for Ethanol (g) = -1409.25 kJ/mol

We must add 44.01 kJ/mol for each mole of H_2O generated

$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_20$

dHc for Ethanol (and everything else, g) = -1409.25 + 3 * 44.01 = -1277.22 kJ/mol

Calculated before = -1277.18 kJ/mol

Very close agreement

Summary

- Chemical reactions cause changes in enthalpy (exothermic and endothermic reactions)
- Hess's Law can be used to estimate enthalpies of reactions using standard enthalpies of formation for the reactants and products
- In the next module, we will look at using extents of reactions to determine enthalpy changes associated with reactions