ABE 201
Biological Thermodynamics 1

Module 15

Enthalpies of Reaction

(Combining Chemical Reactions with 1st Law Energy Balances)

Review

- Expanded definition of enthalpy:
  - Sensible changes due to temperature changes
  - Latent changes due to phase changes
  - Changes due to chemical reactions
- Hess's Law allows us to calculate enthalpies of reactions from balanced stoichiometry using tabulated enthalpies of formation

1st Law Energy Balances

$$\Delta H + \Delta E_k + \Delta E_p \rightarrow Q - W_s$$

Finding Enthalpy Changes

$$\Delta \dot{H} = \Delta \hat{H}_{sensible} \dot{m} + \Delta \hat{H}_{latent} \dot{m} + \Delta \hat{H}_{reaction} \xi$$

Pay attention to units!

Enthalpies of reaction are usually made specific by dividing by <u>moles</u> not kg (i.e. no need to convert ξ to mass/time)

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>

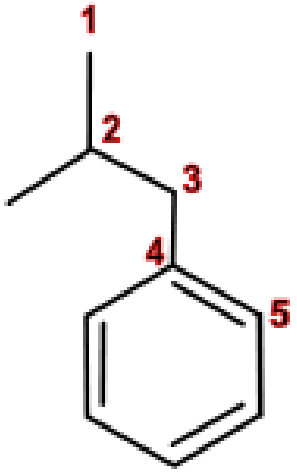
$\Delta\hat{H}_r\,(T,P) > 0,\ Q > 0$ Heat must be <u>added</u>, to maintain constant T: <u>Endothermic</u>

Enthalpies of Formation

Compound	$\Delta H_f'^{o}$(kJ/mol)
ATP	-3616.92
ADP	-2627.24
Citrate	-1513.66
Isocitrate	-1224.7
Ethanol	-290.76
Glucose	-1267.12
Lactate	-688.28
NAD+	-10.26
NADH	-41.38
CO_2 (gas)	-393.50
H_2O (l)	-286.65
Pi	-1299.36

What is an Enthalpy of Formation?

- For organic molecules, estimated using the Benson group additivity method of group contribution



1) C -(C)(H)$_3$ . . . . . 2(-10.20)
2) C -(C)$_3$(H) . . . . . -1.90
3) C -(C$_B$)(C)(H)$_2$ . . . . . -4.86
4) C$_B$ -(C) 5.51
5) C$_B$ -(H) . . . . . 5(3.30)

-5.15 kcal/mole
(-21.6 kJ/mole)

What is an Enthalpy of Formation?

- Also can be determined experimentally

- NIST Chemistry WebBook
  http://webbook.nist.gov/chemistry/

A Note About "Standard" Enthalpies of Formation

- Standard enthalpies of formation (ΔH_f°) is standardized at standard pressure (1 atm), temperature = 25 C, and pH = 0
- Pressure, temperature and pH <u>all</u> affect this value!
- For convenience in biochemical systems, standard enthalpies of formation ($\Delta H_f^{\circ\prime}$) is at standard P and T, but pH = 7
- Note the apostrophe! The two enthalpies are <u>not</u> equivalent!

Estimate Enthalpy of Reaction Using Hess's Law

$$\Delta H_{reaction} = \sum v \Delta H^{'0}_{formation}$$

Where *v* is the stoichiometric coefficient from the balanced reaction equation

Remember: products have $v > 0$ and reactants have $v < 0$

Oxidation of Glucose

What is the standard enthalpy of reaction for the complete oxidation of glucose to carbon dioxide and water (liquid)?

1 glucose + 6 O_2 -> 6 CO_2 + 6 H_2O

ΔH_{rxn} = -1(-1267.12 + 0) + (6*-393.50+ 6*-286.65)

= -2813.78 kJ/mol

Fermentation of Glucose to Ethanol

Glucose is anaerobically fermented to ethanol. What is the enthalpy of reaction? Is this an endo- or exothermic reaction?

1 glucose -> 2 ethanol + 2 CO_2

ΔH_{rxn} = -1(-1267.12 + 0) + (2*-290.76 + 2*-393.50)

= -101.4 kJ/mol

Exothermic reaction!