

## 5.111 Lecture Summary #17

**Readings for today:** Section 7.1 – Spontaneous Change, Sections 7.2 and 7.8 – Entropy, Sections 7.12, 7.13, and 7.15 – Free Energy.

**Read for Lecture #18:** Section 7.16 – Free-Energy Changes in Biological Systems. (Assigned sections in chapter 7 are the same for the 3<sup>rd</sup> and the 4<sup>th</sup> ed.)

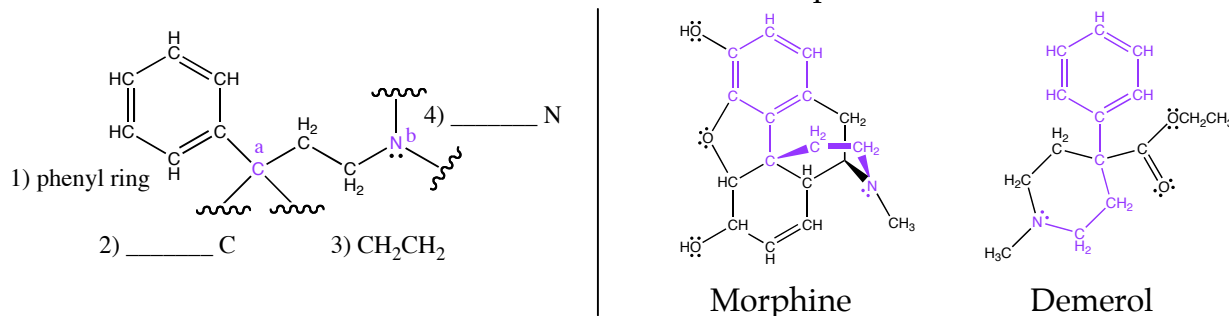
### Topics: Thermodynamics

- I. Enthalpies of reactions: calculating  $\Delta H_r^\circ$  (continued from Lecture #16)
- II. Spontaneous change and free energy
- III. Entropy
- IV. Free energy of formation

Clicker question: review of hybridization

### *Hybridization in complex molecules. Example: the morphine rule*

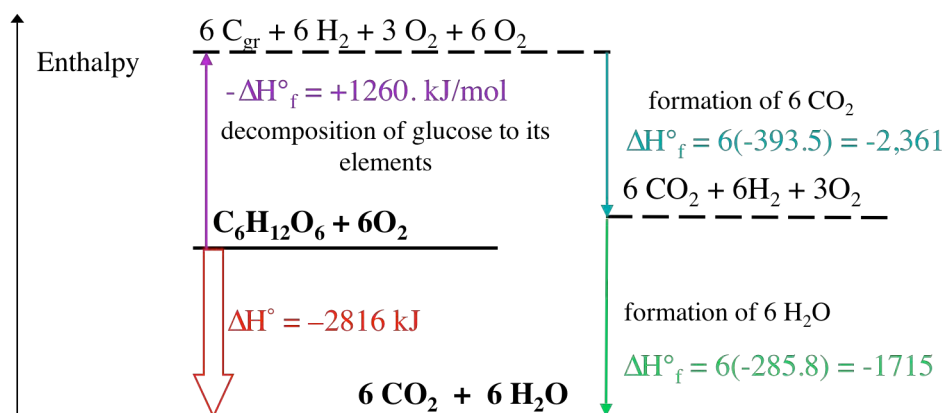
Morphine, a potent and addictive analgesic (“painkiller”), and related molecules share a characteristic set of four features referred to as the morphine rule:



These molecules mimic the action of (and have structural similarities to) endorphins.

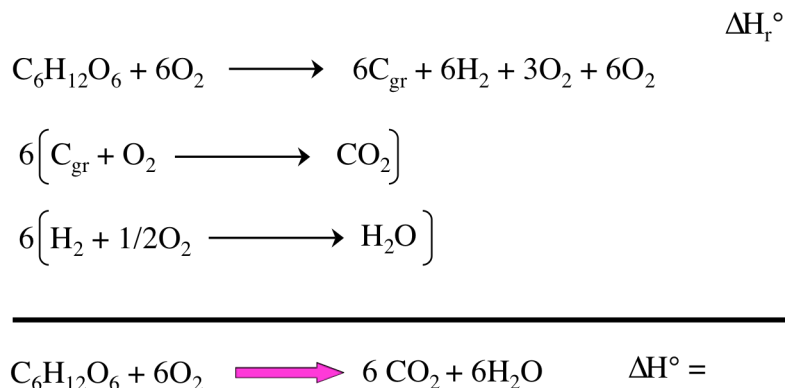
### I. ENTHALPIES OF CHEMICAL REACTIONS (continued from Lecture #16) USING HESS'S LAW TO CALCULATE $\Delta H_r$

Enthalpy is a “STATE” FUNCTION, which means  $\Delta H$  is \_\_\_\_\_ of path.



**Hess's Law:** If two or more chemical equations are added to give another chemical equation, corresponding \_\_\_\_\_ must be added.

$\Delta H^\circ$  for glucose oxidation (all values in kJ):



We have covered 3 methods (so far) to calculate  $\Delta H_r^\circ$ :

1) \_\_\_\_\_ **enthalpies** ( $\Delta H$  or  $\Delta H_B$ )

$$\Delta H_r^\circ = \Sigma \Delta H_B(\text{_____}) - \Sigma \Delta H_B(\text{_____})$$

2) **Standard enthalpies of formation** (\_\_\_\_\_)

$$\Delta H_r^\circ = \Sigma \Delta H_f^\circ(\text{_____}) - \Sigma \Delta H_f^\circ(\text{_____})$$

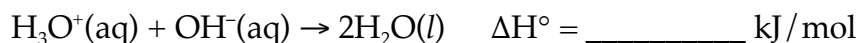
3) **Hess's law**

\*\*\* END OF EXAM #2 MATERIAL \*\*\*

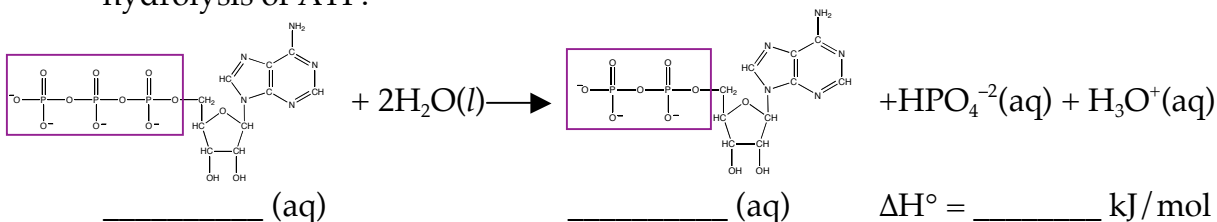
## II. SPONTANEOUS CHANGE AND FREE ENERGY

A **spontaneous change** is a process that, given enough time, occurs without the need for outside intervention.

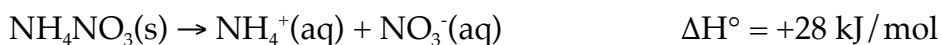
For example, the following reactions are spontaneous at constant pressure:



hydrolysis of ATP:



But so are these ...



Is ΔH the key to spontaneity? \_\_\_\_\_!

Condition for spontaneity under constant P + T involves GIBBS FREE ENERGY, ΔG.

$$\Delta G = \Delta H - T\Delta S$$

where T = temperature and ΔS = change in entropy, a measure of disorder.

ΔG < 0 \_\_\_\_\_ process

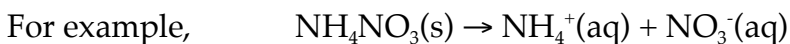
ΔG > 0 \_\_\_\_\_ process

ΔG = 0 equilibrium

Under constant pressure and temperature, a process is spontaneous when ΔG < 0, not necessarily when ΔH < 0. Why?

$$\underbrace{\Delta G}_{\text{Useful work or FREE energy}} = \underbrace{\Delta H - T\Delta S}_{\text{Amount of reaction energy that gets "stuck"}}$$

*Figuring this out was one of the towering achievements of thermodynamics!!*



ΔH<sub>r</sub>° = +28 kJ/mol     ΔS<sub>r</sub>° = +109 JK<sup>-1</sup>mol<sup>-1</sup>

ΔG° = ΔH° - TΔS°

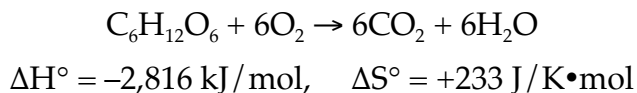
at T = 298 K, ΔG° = \_\_\_\_\_ - \_\_\_\_\_ (\_\_\_\_\_)

ΔG° = \_\_\_\_\_ kJ/mol - \_\_\_\_\_ kJ/mol

ΔG° = \_\_\_\_\_ kJ/mol

$\Delta G^\circ$  is negative, even though  $\Delta H^\circ$  is positive. The reaction is **spontaneous**.

Now consider glucose oxidation at room temperature:



$$\Delta G^\circ = \underline{\hspace{2cm}} - 298(\underline{\hspace{2cm}}) = \underline{\hspace{2cm}} \text{ kJ/mol}$$

$\Delta G^\circ$  more negative than  $\Delta H^\circ$ . This reaction is spontaneous at                      temperatures.

### III. ENTROPY

Entropy,  $S$ , is a measure of the                      of a system.  
 $\Delta S$  = change in entropy.  $\Delta S$  is a state function.

$\Delta S^\circ$  positive  $\Rightarrow$                       in disorder

$\Delta S^\circ$  negative  $\Rightarrow$                       in disorder

Disorder of gas      liquid      solid

In solids, molecules cannot move around freely- they are locked in ordered locations.

Internal degrees of freedom – e.g. multiple molecular configurations, many quantum states that can be occupied - also contribute to entropy

Without calculations, we can predict the sign of  $\Delta S$  for many reactions. For example,  $2\text{H}_2\text{O}_2(l) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$  has a                       $\Delta S$ .

#### Entropy for reactions, $\Delta S_r^\circ$

can be calculated from **absolute** entropies of products and reactants,

$$\Delta S_r^\circ = \Sigma S^\circ(\underline{\hspace{2cm}}) - \Sigma S^\circ(\underline{\hspace{2cm}})$$

where  $S^\circ$  is the absolute standard entropy.

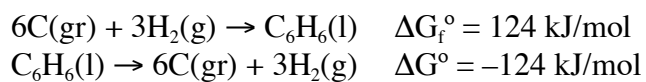
Unlike  $E$  or  $H$ , where the zero can be selected,  $S$  has an absolute zero – the perfect crystal at  $T = 0 \text{ K}$  (perfectly ordered, no disorder at all).

For example, consider the decomposition of hydrogen peroxide.



If  $\Delta G_f^\circ < 0$ , a compound is thermodynamically \_\_\_\_\_ relative to its elements.

If  $\Delta G_f^\circ > 0$ , a compound is thermodynamically \_\_\_\_\_ relative to its elements.



The reverse reaction is spontaneous, but very, very slow!

Free energy tells whether or not a reaction will happen spontaneously, but it tells us \_\_\_\_\_ about the rate of the reaction (for rate information we need chemical kinetics).

To calculate  $\Delta G^\circ$  for a reaction...

$$\Delta G_r^\circ = \Sigma \Delta G_f^\circ(\text{products}) - \Sigma \Delta G_f^\circ(\text{reactants})$$

$$\text{OR} \quad \Delta G_r^\circ = \Delta H_r^\circ - T\Delta S_r^\circ$$

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