5.111 Lecture Summary #35 **Wednesday, December 10, 2014**

Topic: Applying Chemistry Knowledge: A Semester in Review

A look back at the course objectives: My goal is for 5.111 students to have a working knowledge of chemical principles that will allow them to:

- take advanced chemistry classes; carry out a UROP in the chemistry department; employ chemistry in research outside of the chemistry department
- appreciate how chemistry is used to solve real-world problems
- make informed decisions about personal health, environmental and energy issues, and science policy
- advance science and engineering through the application of chemical principles.

A look back at the course topics:

Atomic theory
Periodic Table Trends
Bonding
Structure of Molecules

} Basic properties of matter

Thermodynamics
Chemical Equilibrium & Solubility
Acid-Base
Oxidation-Reduction
Transition Metals
Kinetics

} How matter reacts

Let's review selective topics using carbon dioxide as a case study.
CO_2 is a waste product of the combustion of fossil fuels. It is a greenhouse gas and thus a player in global warming. It also contributes to the acidification of our oceans. We need to remove it from our environment, but what if we can do one better; use it to make biofuels?

Approaches Include: designing small molecule catalysts to convert CO_2 to biofuels and re-engineering biological CO_2 fixation pathways, but before either we do either, we must understand the basic properties and reactivity of our reactant – CO_2.

<u>Basic Properties of CO_2</u>

BONDING. How is C bonded to O in CO_2? Let's use Lewis structures to make a prediction.

STRUCTURE. What is the geometry a CO_2 molecule? And what is its polarity?

Reactivity of CO_2

THERMODYNAMIC. Is CO_2 stable or unstable compared to its elements?

$$C_{gr}\ (s) + O_2\ (g) \rightarrow CO_2\ (g)$$

To answer this question, one needs to know ________________.

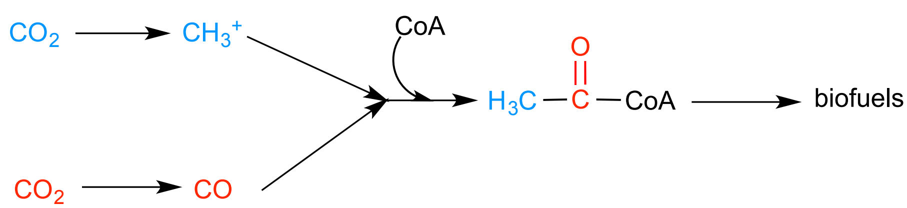
Given that ____________ is - 394.39 kJ/mol, CO_2 is ______________________.

Let's review what we have learned about CO_2. It has _____________ bonds, which typically means a big bond dissociation energy.

It is ______________________ , ______________________ and ______________________.

With knowledge of our reactant in hand, we next seek to understand how nature "fixes" carbon dioxide (i.e. converts one-carbon units into multi-carbon units). There are six pathways that fix CO_2. One pathway of interest is the microbial acetogenesis pathway.

In acetogenesis, two molecules of CO_2 are added to coenzyme A (CoA) to make acetyl-CoA (a precursor to several multicarbon molecules that can serve as biofuel).



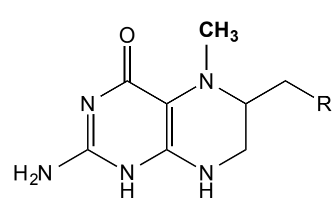
Before scientists can harness microbial acetogenesis to make biofuels, they must understand how it works. *Does acetogenesis require redox reactions? Are some of the reactions acid-base catalyzed? Are transition metals involved? What are the challenging or rate-limiting steps? Which factors influence the chemical equilibrium of each reaction?*

OXIDATION-REDUCTION. Is CO_2 being reduced or oxidized?______________________.

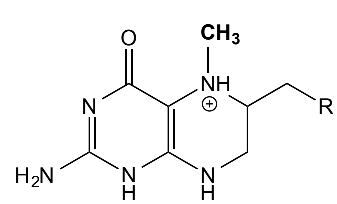
CO_2 is converted to CH_3^+ through the action of five different enzymes. How are these carbon units transferred in an efficient manner from enzyme to enzyme? Answer: by attaching them to B vitamin folate (or folic acid) and having the folate shuttle between enzymes.

Folate is a wonderful vehicle for transferring one-carbon units, but after CO_2 is fully reduced to a methyl moiety (CH_3^+), how is it removed from the folate?

ACID-BASE. Removal of CH_3^+ from folate requires that folate is protonated. If the pK_a of folate is 4.8, how much will be protonated at physiologically pH?

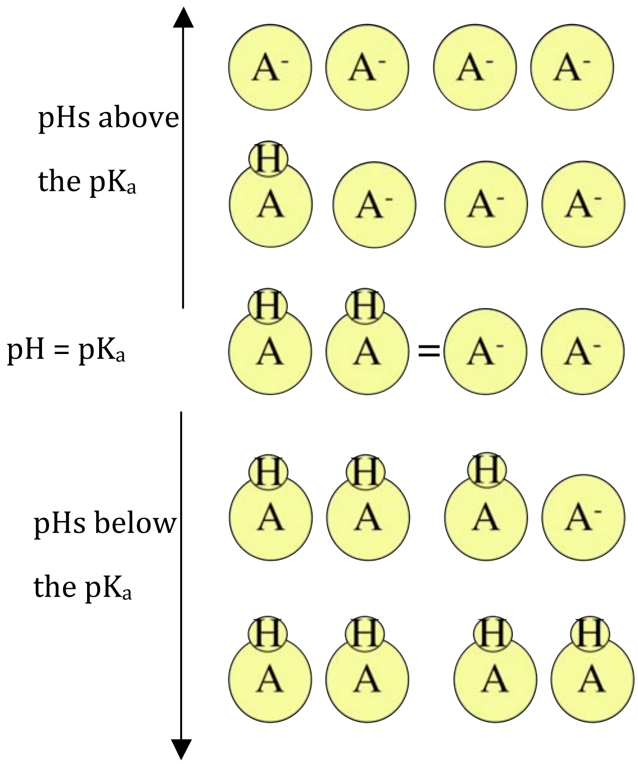


Deprotonated



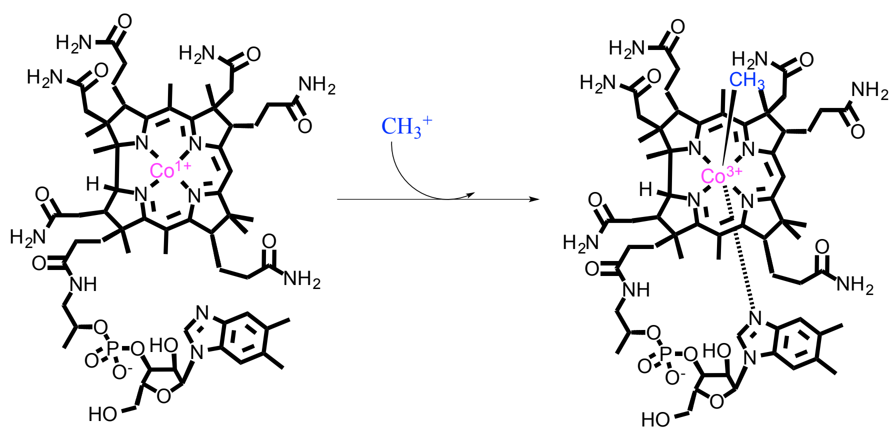
Protonated

$$pH = pK_a - \log\left(\frac{[HA]}{[A^-]}\right) \qquad 7.4 = 4.8 - \log\left(\frac{[HA]}{[A^-]}\right) \qquad \frac{[HA]}{[A^-]} =$$



Removal of the methyl group is challenging given the low pK_a of the folate.
How is this challenge overcome? Answer: nature uses a vitamin B_{12} dependent enzyme.

TRANSITION METALS AND CATALYSIS. Methyl transfer from folate has a big E_a barrier. To catalyze this reaction, the highly reactivity +1 oxidation state of an enzyme-bound vitamin B_{12} is used. Enzyme-bound B_{12} removes the methyl group from folate, forming methylB_{12}.



dcount =

Geometry around Co _____________

dcount =

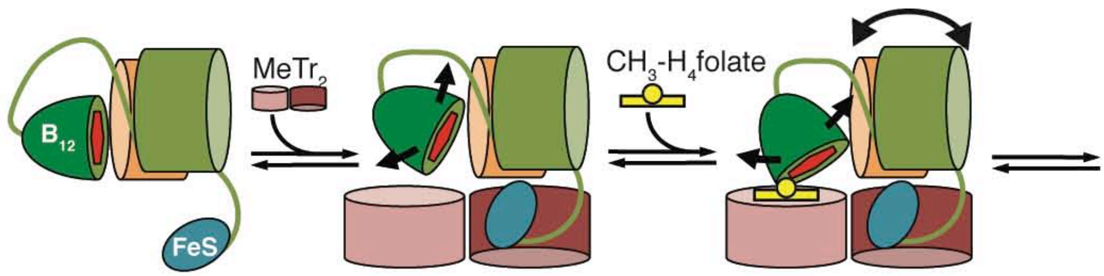
Geometry around Co_________________

The corrin ring is a ___________dentate ligand

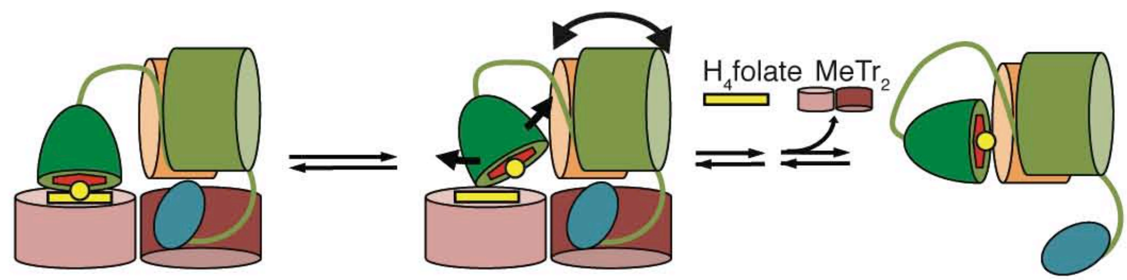
CHEMICAL EQUILIBRIUM
The B_{12} enzyme exists in both OPEN and CLOSED conformations. These conformations are in equilibrium with each other.

The CLOSED state protects the highly reactive B_{12} and the OPEN state allows the B_{12} enzyme to accept the methyl group from a folate molecule, which is bound to a dimeric methyl transferase enzyme ($MeTr_2$).

The OPEN state also allows for the B_{12} enzyme to donate the methyl group to the enzyme that makes acetyl-CoA (acetyl-CoA synthase).



CLOSED state   Opening   OPEN state to accept methyl



Methyl transfer   Closing   CLOSED state

Next, the B_{12} enzyme must open up again to transfer the methyl group to the enzyme that makes acetyl-CoA. The equilibrium of conformers of the B_{12} enzyme is shifted when the other enzymes and/or the other reactants (like folate) bind.

Enzymes are dynamic.
Chemistry is dynamic.
CHEMISTRY IN SOLUTION IS COOL!!!!!
AND CAN SAVE THE PLANET!!!!!!!!

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