No Analytical Crib
August 25, 2018
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No Biochemistry Crib
August 25, 2018
Written by Professor Tantama
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No Inorganic Crib
August 25, 2018
Written by Professor McMillin
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A. i) Thermodynamically feasible if

\[
\frac{Pt^{2+}/Pt}{0.96 \text{ PtCl}_4^-/Pt} \quad \frac{Cu^{2+}/Cu}{0.0} \quad \frac{Fe^{2+}/Fe}{\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{ }\text{
Dynamic covalent chemistry (DCvC) is a synthetic strategy employed by chemists to make complex supramolecular assemblies from discrete molecular building blocks. DCvC has allowed access to complex assemblies such as covalent organic frameworks, molecular knots, polymers, and novel macrocycles. It presents a unique opportunity when it comes to the plastic pollution—a globally alarming challenge we face.

1) (25 points) DCvC is a branch of supramolecular chemistry, which features the dynamic nature.
   a) (5pts) How does DCvC fundamentally differ from supramolecular chemistry involving non-covalent interactions?
   b) (5pts) How do you confirm reversibility in DCvC? What are the methods commonly used?
   c) (10 pts) Please list five major types of dynamic covalent reactions (i.e. C-N bond, C-C bond, C-O bond, B-O bond and cyclic reactions). (Reactions that appear in this rest cannot be used)
   d) (5 pts) please also list five types of non-covalent interactions that are frequently used for supramolecular chemistry.

a) DCvC involves covalent bonds which are typically much stronger than non-covalent interactions.

b) Two methods are commonly employed. The first method is termed **dual entry - point analysis**. A dynamic system is being generated from two different systemic starting compositions while maintaining the overall ratio of the building blocks. Pathway - independence is the defining characteristic of a system at equilibrium. Thus, if the same component distribution is obtained regardless of entry point, it provides evidence that the system is under thermodynamic control. This type of test constitutes the most robust and well - utilized application for testing new dynamic systems and dynamic covalent bonds.

Another useful way to probe equilibration is **the stationary state perturbation method**. Here, an initial dynamic system is generated under the conditions of interest and allowed to evolve until a point is reached where the system composition no longer changes. Thereafter, another exchange partner is added, and the system is again allowed to settle into equilibrium. If the new partner has been incorporated into the dynamic system and the initial component distribution has changed, it provides a good indication that the system originally was at equilibrium.

NMR analysis of the reaction product is frequently used.

c) Imine metathesis

\[
\begin{align*}
R_1 & \equiv N^\equiv R_2 + \equiv N^\equiv R_1 & \text{↔} & \equiv N^\equiv R_1 + \equiv N^\equiv R_2 \\
\text{Carbene dimerization} & \text{↔} & \text{↔}
\end{align*}
\]
Thioester exchange

Disulfide exchange

Dioxaborolane metathesis

d) Hydrogen bonding, halogen bonding, dipole-dipole moment, anion-π interaction, π-π interaction, metal-ligand interaction


a) (15 pts) Fast and reversible dynamic covalent C–C/C–N exchange takes place without catalyst in nonpolar solvents between barbiturate-derived Knoevenagel (Kn) compounds and imines. Please write a detailed reaction mechanism with an arrow drawing and key intermediates.

b) (10 pts) Write the key steps and intermediates for synthesis of the following compound.

a) (5 pts) What are the features for a vitrimer?

b) (5 pts) What is the difference between boronic ester transesterification and dioxaborolane metathesis?

c) (5 pts) Can you design a series of experiments to elucidate the mechanism for dioxaborolane metathesis?

a) Vitrimers behave like permanently crosslinked materials at service temperatures, are insoluble at all temperatures, but can still flow when heated. Vitrimers consist of a polymer network that is able to change its topology without decreasing its connectivity thanks to exchange reactions, which maintain constant the number of chemical bonds and cross-links. At high temperatures, exchanges are fast, and the material can be processed. By cooling, the shape is fixed either by quenching the exchange reaction or the motion of polymer molecules through glass transition (Tg) or crystallization.

5) (20 pts) The world’s mounting plastic trash crisis is hard to solve because it has many dimensions: social, technical, and economic. But because chemistry brought the problem into the world, it doesn’t seem unreasonable to look to chemistry for a solution (*c&en*, June 15, 2018). Thermoplastics are light, tough, and easy to process but are limited by their lower strength, structural stability at high temperature, abrasion, and solvent resistances. Unlike thermoplastics, such as polyethylene, polystyrene, and polypropylene that can be melted and
Dynamic Covalent Chemistry: Principles, Reactions, and Applications molded into new forms, thermoset polymers harden irreversibly thanks to covalent cross-linkers that bridge polymer strands but reduce the ability of thermoplastics to flow when heated. As a result, the synthesis, processing, and recycling of cross-linked polymers, called thermosets, are complex and costly.

Using DCvC to design recyclable thermoset polymers. Two criteria shall be met. First, polymers backbones are solely made of carbon-carbon single bonds. Second, the chemistry you choose has to make the resulting thermoset polymers processable like thermoplastics. So that there is no need to change neither the equipment nor the mass production speed currently used. (Note: you can not choose the chemistry in question 3 and 4)

Many such polymers can be designed. Two examples are given below.

a) Use dynamic boronic ester bonds

\[
\begin{align*}
\text{B-O} & + \text{HO-} \rightarrow \text{B-OH} \\
\text{X} & = \text{CH}_2\text{NR}_2, \text{Fast} \\
\text{X} & = \text{H}, \text{Slow} \\
\text{B-O} & + \text{HO-} \rightarrow \text{B-OH}
\end{align*}
\]

\(=\) Telechelic Boronic Ester \(=\) 1,2-diol

b) Reversible Diels-Alder cycloaddition reaction
Diels-Alder reaction
T = r.t. to 90 °C

Retro-Diels-Alder reaction
T > 120 °C
\[ E = \frac{\hbar^2 \nu^2}{8mL^2} \quad m_e = 9.1 \times 10^{-31} \text{ kg} \quad m_p = 1.7 \times 10^{-27} \text{ kg} \]
\[ \hbar = 6.6 \times 10^{-34} \text{ Js} \quad a_0 = 0.0529 \times 10^{-9} \text{ m} \]

1) (10 points) Use the above expression for the energy of a 1 dimensional particle in a box to obtain an expression for the energy of a particle in a 3 dimensional box, with sides of length \( L_x, L_y \) and \( L_z \), and quantum numbers, \( n_x, n_y, \) and \( n_z \).

\[ E = \frac{\hbar^2}{8m} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right) \]

2) (10 points) What are the three quantum numbers of the first excited state of a 3 dimensional particle in a box whose sides have lengths of \( L_x, L_y = 1.5 \ L_x \), and \( L_z = 2 \ L_x \).

\[ n_x, n_y, n_z = 1, 1, 2 \]

3) (10 points) Given that the first excited state of a hydrogen atom has an energy that is \( 1.64 \times 10^{-18} \text{ J} \) above the ground state, determine the frequency of the corresponding optical absorption line (expressed in \( \text{s}^{-1} \) units).

\[ \Delta \epsilon = h \nu \quad \text{so,} \quad \nu = \frac{\Delta \epsilon}{h} = 2.5 \times 10^{15} \text{ s}^{-1} \]

4) (20 points) Using the above optical transition energy, and assuming that a hydrogen atom can be treated as an electron confined to a 3 dimensional cube of volume \( d^3 \) (\( \text{nm}^3 \)), estimate \( d \) (expressed in \( \text{nm} \) units).

\[ \Delta \epsilon = \epsilon_{112} - \epsilon_{111} = \frac{6h^2}{8m_e d^2} - \frac{3h^2}{8m_e d^2} = \frac{3h^2}{8m_e d^2} = 1.64 \times 10^{-18} \]

\[ d = \sqrt{\frac{3 \times h^2}{1.64 \times 10^{-18} \times 8 \times m_e}} \approx 0.33 \times 10^{-9} \text{ nm} = 0.33 \text{ nm} \]

5) (20 points) Given that the bond length of \( \text{H}_2 \) is \( R = 0.074 \text{ nm} \), and assuming that an \( \text{H}_2 \) molecule may be treated as two electrons confined to a box whose sides have length \( d \), \( d \), and \( R+d \), estimate the bond formation energy of \( \text{H}_2 \) (expressed in \( \text{J} \) units).

\[ \Delta \epsilon = \epsilon_{H_0} - 2 \epsilon_H = 2 \left( \frac{h^2}{8m_e} \right) \left[ \frac{2}{d^2} + \frac{1}{(d+R)^2} \right] - 2 \left( \frac{3h^2}{8m_e d^2} \right) = 2 \left( \frac{h^2}{8m_e} \right) \left[ \frac{1}{(d+R)^2} \right] \approx -3.7 \times 10^{-19} \text{J} \]

Note that each H atom contributes 1 electron to \( \text{H}_2 \), so the ground state of \( \text{H} \) has two electrons.

6) (30 points) Estimate the density at which solid hydrogen would undergo an insulator to metal transition (express the density in atoms per \( \text{nm}^3 \) units).

The insulator to metal transition might be expected to occur with the boxes overlap.

\[ \rho = \frac{N}{V} \approx \frac{1}{d^3} \approx 28 \text{ atoms per cubic nm} \]