PART I: Carbon Chemistry and Molecular Design

1. (5 points each) Consider the peptide:

phe–glu–ser–pro–leu–gly–trp

a) Which residue will exhibit the + charge (at pH ~7)?

phe

b) To which residue will the -ser- residue hydrogen bond if the peptide forms an α - helix?

trp

c) Give the sequence of bases that will code for this peptide in m - RNA.

UUC - GAA - AGC - CCA - UUA - GGA - UGG

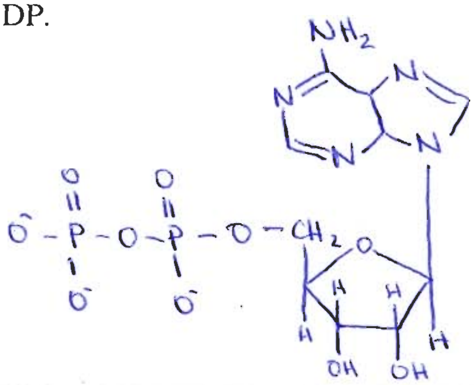
d) Give the sequences of bases that will produce the above m - RNA sequence in the transcription process.

AAG - CTT - TCG - GGT - AAT - CCT - ACC

e) What are the 3 main differences between DNA and RNA?

1. The DNA backbone is made from the sugar deoxyribose while in RNA, ribose is used.
2. DNA uses the nucleic acid thymine while RNA has uracil.
3. DNA is double-stranded while RNA is single-stranded.

f) Draw the structure of ADP.



2. **(10 points)** In a combustion experiment, 3.21 g of a hydrocarbon formed 4.48 g of water and 9.72 g of carbon dioxide. Deduce its empirical formula and state whether it is likely to be an alkane, an alkene, or an alkyne. Explain your reasoning.

$$4.48\text{g } H_2O \cdot \frac{1\text{mol}}{18.02\text{g}} = 0.25 \text{ mol } H_2O \rightarrow 0.50 \text{ mol H}.$$

$$9.72\text{g } CO_2 \cdot \frac{1\text{mol}}{44.01\text{g}} = 0.22 \text{ mol } CO_2 \longrightarrow 0.22 \text{ mol C}$$

$$\frac{\text{mol C}}{\text{mol H}} = \frac{0.22}{0.50} = 0.44 \sim 4/9 \quad \boxed{C_4H_9}$$

The molecular formula could be C_8H_{18} which is an alkane satisfying the formula C_nH_{2n+2}.

3. **(10 points)** A hydrocarbon is 90% carbon by mass and 10% hydrogen by mass and has a molar mass of 40 g·mol^{-1}. It decolorizes bromine water, and 1.46 g of the hydrocarbon reacts with 1.60 L of hydrogen (measured at STP) in the presence of a nickel catalyst. Write the molecular formula of the hydrocarbon and the structural formulas of two possible isomers.

assuming 100g,

$$90\text{g} \cdot \frac{1\text{mol}}{12.01\text{g C}} = 7.49 \text{ mol C}$$

$$10\text{g} \cdot \frac{1\text{mol}}{1.01\text{g H}} = 9.90 \text{ mol H}$$

$$\frac{7.49 \text{ mol C}}{9.90 \text{ mol H}} = 0.76 \sim 3/4 \quad \boxed{C_3H_4}$$

molar mass: $3(12.01) + 4(1.01) = 40\text{g/mol}$ ∴ C_3H_4 is both the molecular & empirical formula

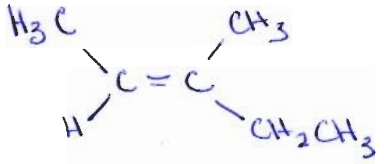
$$1.46\text{g } C_3H_4 \cdot \frac{1\text{mol}}{40\text{g}} = 0.0365 \text{ mol } C_3H_4$$

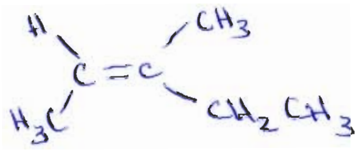
$$\text{mol H} = \frac{PV}{RT} = \frac{(1\text{atm})(1.6\text{L})}{(0.08206 \frac{\text{L atm}}{\text{mol K}})(273\text{K})} = 0.0714 \text{ mol H}$$

$$\frac{0.0714 \text{ mol H}}{0.0365 \text{ mol } C_3H_4} \sim 2 \therefore 2\ \pi \text{ bonds}$$

$$\boxed{HC{\equiv}C-CH_3 \quad \& \quad H_2C=C=CH_2}$$

4. (9 points) Give the systematic name of the following compound. If geometrical isomers are possible, write the names of each one: $CH_3CH{=}C(CH_3)CH_2CH_3$





cis-3-methyl-2-pentene & trans-3-methyl-2-pentene

5. (2 points each) Classify each of the following reactions as (1) an addition reaction, (2) a nucleophilic substitution reaction, (3) an electrophilic substitution reaction, or (4) a condensation reaction:

a) the reaction of benzene with Br_2 and FeBr

(3) electrophilic substitution

b) the polymerization of the amino acid glycine

(4) condensation

c) the hydrogenation of butyne

(1) addition

d) the polymerization of styrene, $CH_2CHC_6H_5$, by tertiary butyl hydroperoxide, $(CH_3)_3COOH$

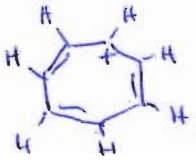
(1) addition

e) the reaction of methylamine with butanoic acid

(4) condensation

6. **(5 points each)** Consider the cycloheptatrienyl cation ($C_7H_7^+$):

a) Is it aromatic or alaphatic? Explain.



Aromatic. There are 4n+2 conjugated π electrons

b) Why might you expect benzene to be more stable than this molecule?

Benzene has exactly 120° angles for sp^2 hybridization.

c) What characteristic type of reaction would you expect an aromatic molecule to undergo?

electrophilic substitution

7. **(4 points each)** Describe the four universal features of living systems (give one sentence of detail for each).

a) Living systems use the same 20 amino acids as the building blocks for all proteins.

b) They follow the same genetic coding sequence of DNA → RNA → protein.

c) They use the same energy source/storage of ADP ↔ ATP.

d) Living systems display handedness such as only having D-sugars.

PART II: Cumulative

1. (5+10+10 points) Methanol, CH_3OH, is a clean-burning liquid fuel being considered as a replacement for gasoline.

	Molar mass, M ($g\cdot mol^{-1}$)	Enthalpy of combustion, $\Delta H_c°$ ($kJ\cdot mol^{-1}$)	Enthalpy of formation, $\Delta H_f°$ ($kJ\cdot mol^{-1}$)	Free energy of formation, $\Delta G_f°$ ($kJ\cdot mol^{-1}$)	Molar heat capacity, $C_{P,m}$ ($J\cdot K^{-1}\cdot mol^{-1}$)	Molar entropy, $S°$ ($J\cdot K^{-1}\cdot mol^{-1}$)
CH_3OH~~(l)~~(g)	32.04	–726	–238.86	–166.27	81.6	126.8

a) Calculate the theoretical yield in kilograms of CO_2 produced by the combustion of 1.00 L of methanol (of density 0.791 $g\cdot cm^{-3}$) and compare it with the 2.16 kg of CO_2 generated by the combustion of 1.00 L of octane. Which fuel contributes more CO_2 per liter to the atmosphere when burned? [Assume a combustion temperature of 2500K.]

$$2CH_3OH(g) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(g)$$

$$1L \cdot \frac{1000mL}{1L} \cdot \frac{0.791g}{1mL} = 791g\ CH_3OH$$

$$791g\ CH_3OH \cdot \frac{1mol}{32.05g} = 24.7\ mol\ CH_3OH$$

$$24.7\ mol\ CH_3OH \cdot \frac{2mol\ CO_2}{2mol\ CH_3OH} \cdot \frac{44.01g\ CO_2}{1mol\ CO_2} = 1086.2g \rightarrow \boxed{1.09\ kg\ CO_2}$$

Octane contributes more CO_2 per liter to the atmosphere than methanol when burned.

b) Calculate the energy equivalent (EE) of methanol.

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

$$\Delta G = (-726\ kJ/mol) - (2500K)(0.1268\ kJ/mol\,K)$$

$$\Delta G = -1043\ kJ/mol$$

$$EE = (-1043\ kJ/mol)\left(\frac{1mol}{32.05g}\right)\left(\frac{1000g}{1kg}\right) = \boxed{3.25 \times 10^4\ kJ/kg}$$

c) Calculate the maximum total work that can be obtained by burning 1.00 L of methanol at 2500K.

$W_{total} = \Delta G + W_{PV}$

$W_{PV} = -P\Delta V = -\Delta nRT$ $\qquad \Delta n = \frac{1}{2}(24.7) = 12.35$

$= -(12.35\,mol)(8.314\ J/mol\,K)(2500K)$

$= -256{,}694\ J \rightarrow -256.7\ kJ$

$W_{total} = (-1043\ kJ/mol)(24.7\ mol) + (-256.7\ kJ)$

$\approx \boxed{-2.56 \times 10^{4}\ kJ}$

2. (5+10+10+5 points) Gold, Silicon, and Diamond are prototypes for metals, semiconductors, and insulators, respectively.

a) Sketch and label their energy band diagrams, specifying the band gaps (eV)?

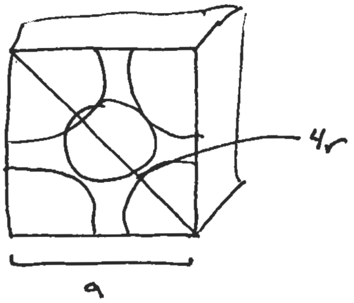
b) Describe their respective crystal structures.

Gold: ccp (or fcc)

Silicon: "diamond lattice" - fcc with atoms in ½ tetrahedral holes

Diamond: "diamond lattice" - fcc with atom in ½ tetrahedral holes

c) Calculate the packing fraction for the gold lattice.



ccp

$a^2 + a^2 = (4r)^2$

$a = \sqrt{8}r$

$a^3 = \underline{8^{3/2} r^3} = V_{cube}$

$V_{sphere} = \frac{4}{3}\pi r^3$

4 spheres/cube

$V_{spheres\ total} = \underline{4 \times \frac{4}{3}\pi r^3}$

$$\text{Packing Fraction} = \frac{\frac{16}{3}\pi r^3}{8^{3/2} r^3} = .74$$

d) Explain why gold is so inert.

- Valence shells are filled
- Filling of 4f orbitals reduces shielding of outer electrons, causing the radius to decrease and reduce reactivity. This is the lanthanide contraction.

3. **(15 points)** HO_2 is a highly reactive chemical species that plays a role in atmospheric chemistry. The rate of the gas-phase reaction

$$HO_2(g) + HO_2(g) \rightarrow H_2O_2(g) + O_2(g)$$

is second order in $[HO_2]$, with a rate constant at 25°C of 1.4×10^9 L mol^{-1} s^{-1}. Suppose some HO_2 with an initial concentration of 2.0×10^{-8} M could be confined at 25°C. Calculate the concentration that would remain after 1.0 s, assuming no other reactions take place.

$$\text{Rate} = k[HO_{2(g)}]^2$$

Second-order rate law:

$$[A]_t = \frac{[A]_0}{1 + kt[A]_0}$$

$$= \frac{2.0 \times 10^{-8} M}{1 + (1.4\times10^9 \frac{L}{mol \cdot s})(1 s)(2.0 \times 10^{-8} M)}$$

$$= \underline{6.9 \times 10^{-10} M}$$

4. **(5 points each)** Consider the Fullerene C_{84}:

a) The number of pentagons is 12.

b) The number of hexagons is 32.

c) The number of dangling bonds is 0.

d) The hybridization of each carbon is sp^2.

e) Is this molecule superaromatic? Explain.

Yes, follows the formula 60 + 6n where n = 4

5. (10+5+5 points) Ethane dissociates into methyl radicals at 700.°C with a rate constant $k = 5.5 \times 10^{-4}\ s^{-1}$.

a) Determine the rate constant at 500.°C, given that the activation energy of the reaction is 384 $kJ \cdot mol^{-1}$.

$$\ln \frac{k'}{k} = \frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T'}\right)$$

$$\ln \frac{k'}{5.5 \times 10^{-4}\ s^{-1}} = \frac{384\ kJ\ mol^{-1}}{.008314\ kJ\ mol^{-1}\ K^{-1}}\left(\frac{1}{973K} - \frac{1}{773K}\right)$$

$$k' = 2.5 \times 10^{-9}\ s^{-1}$$

b) What type of reaction would ethane be expected to exhibit with bromine molecules in the gas phase?

substitution

c) How would you prepare ethylene (ethene) from ethane?

react with Cr_2O_3

6. (10+10+5+15 points each) The body functions as a kind of fuel cell that uses oxygen from the air to oxidize glucose at a temperature of 37°C:

$$C_6H_{12}O_6(aq) + 6\,O_2(g) \rightarrow 6\,CO_2(g) + 6\,H_2O(l)$$

	Molar mass, M (g·mol^{-1})	**Enthalpy of combustion, $\Delta H_c°$ (kJ·mol^{-1})**	**Enthalpy of formation, $\Delta H_f°$ (kJ·mol^{-1})**	**Free energy of formation, $\Delta G_f°$ (kJ·mol^{-1})**	**Molar heat capacity, $C_{P,m}$ (J·K^{-1}·mol^{-1})**	**Molar entropy, $S°$ (J·K^{-1}·mol^{-1})**
$C_6H_{12}O_6$(s), glucose	180.15	–2808	–1268	–910	–	212
$C_6H_{12}O_6$(aq)	180.15	–	–	–917	–	–
$C_6H_{12}O_6$(s), fructose	180.15	–2810	–1266	–	–	–
$C_{12}H_{22}O_{11}$(s), sucrose	342.29	–5645	–2222	–1545	–	360

a) During normal activity, a person uses the equivalent of about 10 MJ of energy a day. Assume that this value represents ΔG, and assuming that all the energy that we use arises from the reduction of O_2 in the glucose oxidation reaction, estimate the resulting average electrical current flowing through your body in the course of a day.

$$P = IV$$

$$I = \frac{P}{V}$$

$$= \frac{1160\,W}{43\,V} \quad \text{(from parts b \& d)}$$

$$= \underline{27A}$$

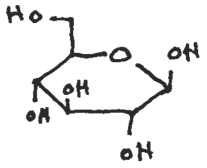
b) Calculate the power (watts) produced by this process.

$$\text{Power} = \frac{\text{Energy}}{\text{time}} = \frac{\Delta G}{t}$$

$$= \frac{10^7\ \text{J}}{(24\,\text{h})(60\,\text{min})(60\,\text{s})}$$

$$= \underline{1160\ \text{W}}$$

c) Draw the structure of the ring form of glucose.



d) Calculate the cell voltage that could be obtained from a fuel cell employing this reaction under the above conditions.

$$\Delta G = -nFE^\circ$$

$$10^7 J = -(24 \text{mol } e^-)\left(\frac{96{,}500 \text{ C}}{\text{mol } e^-}\right)E^\circ$$

$$\underline{E^\circ = 43 V}$$

Note: n comes from oxidation of O_2: $0 \rightarrow -2$ oxidation state × 2 oxygen × 6 moles

Also, this is actually <u>NOT</u> the way to do the problem correctly, but no one got the right answer so we accepted full credit for the above. Right way:

$\Delta G_{day} = 10^7 J$, $\Delta G^\circ_{rxn} \approx \Delta H^\circ_{combustion}$ since $\Delta S \approx 0$ (6 moles gas on each side)

So $\Delta G_{rxn} = -2808 \text{ kJ/mol} \Rightarrow \frac{10^7 J}{2.9 \times 10^6 J} = 3.6$ mol glucose oxidized per day, so $\boxed{\Delta G = 3.6 \left(2808 \frac{kJ}{mol}\right)}$

now plug into $\Delta G = -nFE^\circ$

$$\underline{E^\circ = 4.4 \text{ mV}}$$

7. **(10+5+10 points)** Given the following mechanism for catalysis of a substrate (S) by an enzyme (E) to yield a product (P):

$$E + S \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} ES$$

$$ES \xrightarrow{k_2} E + P$$

a) Derive the expression for the rate of formation of P in terms of <u>total</u> enzyme concentration $[E]_o = [E] + [ES]$ and the Michaelis constant $K_m = \frac{k_1 + k_2}{k_1}$.

$$\text{Rate} = \frac{d[P]}{dt} = k_2[ES]$$

Steady-state: $\frac{d[ES]}{dt} = 0 = k_1[E][S] - k_{-1}[ES] - k_2[ES]$

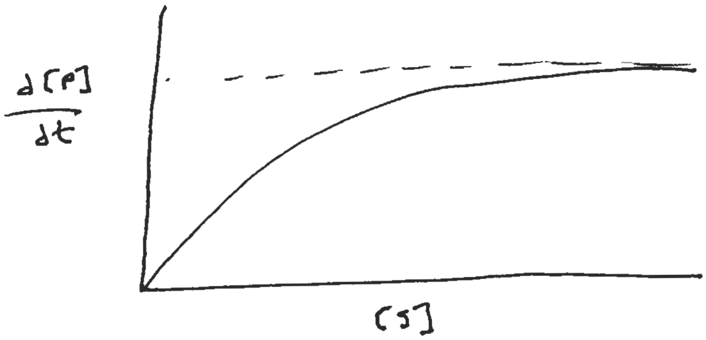
$$[ES] = \frac{k_1[E][S]}{k_2 + k_{-1}}$$

in terms of $[E]_o = [E] + [ES] \Rightarrow k_1[E]_o[S] - k_{-1}[ES] - k_2[ES] - k_1[ES][S]$

$$[ES] = \frac{k_1[E]_o[S]}{k_1[S] + (k_{-1} + k_2)} = \frac{[E]_o[S]}{[S] + K_m}$$

$$\text{so} \quad \underline{\text{Rate} = \frac{k_2[E]_o[S]}{[S] + K_m}}$$

b) Sketch a graph of the product formation rate versus substrate concentration.



c) The rates of enzyme catalysis can be lowered by the presence of inhibitor molecules I, which bind to the active site of the enzyme. This adds the following additional step to the reaction mechanism:

$$E + I \underset{k_{-3}}{\overset{k_3}{\leftrightarrow}} EI \qquad \text{(fast equilibrium)}$$

Determine the effect of the presence of inhibitor at total concentration $[I]_0 = [I] + [EI]$ on the rate expression for formation of products derived at the end of this chapter.

$$[E] = [E]_0 - [ES] - [EI] = [E]_0 - [ES] - \frac{k_3}{k_{-3}}[E][I]$$

$$[E] = \frac{[E]_0 - [ES]}{1 + \frac{k_3}{k_{-3}}[I]}$$ sub into expression for [ES]

$$[ES] = \frac{k_1 [E]_0 [S]}{k_1 [S] + \left(1 + \frac{k_3}{k_{-3}}[I]\right)(k_{-1} + k_2)}$$ sub into Rate = $k_2[ES]$

* only affects expression for [E] . . .

8. (10 points) Describe the two classes of explosions demonstrated in class and give an example of each.

1. Chain Reactions (free radical chain mechanism)

i.e. $H_2 + O_2 \rightarrow \ldots$ (any combustion rxn)

$CH_4 + O_2 \rightarrow \ldots$

2. Thermal

$k(T) \propto e^{-E_a/RT}$

i.e. $CS + NO \rightarrow \ldots$

(any solid-state explosion)

9. (10 points) The typical potassium ion concentration in the fluid outside a cell is 0.0050 M, whereas that inside a muscle cell is 0.15 M.

In *active transport*, cells use free energy stored in ATP to move ions in the direction opposite their spontaneous direction of flow at body temperature (37°C). Calculate the cost in free energy to move 1.00 mol K+ through the cell wall by active transport. Assume no change in K+ concentrations during this process. State any other assumptions.

$\Delta G = -RT \ln Q$

$= -8.314\ J\,mol^{-1}K^{-1}\ (310\ K) \ln\left(\frac{.15\ M}{.0050\ M}\right)$

$= -8766\ J\,mol^{-1}$

to move 1 mol $\Rightarrow \left(8766\ \frac{J}{mol}\right)(1\ mol) = \underline{8800\ J}$

assumptions: constant P + many others (no pts. taken off here)