Key

Chem 113000-2 Spring 2022 Final Review

The following questions cover content from the entire quarter but in no way represent everything that you can be tested on. These questions should be supplemented with understanding of all homework problems, discussion worksheet problems, as well as the 3 midterms. Furthermore, the only additional material that should be needed to complete these questions is a calculator and a periodic table (in addition to the constants/values provided on this front page). While a formula sheet will be provided for your final, it is best to know as many of the equations.

Some useful constants:

1. K_{sp} for $PbCl_2$ is 1.17×10^{-5}
2. $R = 8.314$ J/mol K
3. $F = 96485$ C/mol e

Reduction	$E°$ [V]
Fe^{3+}| Fe	-0.036
Li^{+}| Li	-0.30
Mn^{2+}| Mn	-1.17
Al^{3+}| Al	-1.66
MnO_2| Mn^{2+}	1.21
Pb^{2+}| Pb	-0.13
Hg^{2+}| Hg	0.85
Cu^{2+}| Cu	0.34
Rh^{3+}| Rh	0.800

1. For the following questions, select the *one* correct answer for each multiple choice questions.

(a) Which of these types of decay results in a change in the mass number of the parent nuclide?

A) α decay
B) β decay
C) γ decay
D) Electron capture decay
E) Positron emission decay

(b) Which of the following pairs of name and formula is matched correctly?

A) Beryllium bisulfite, $Be(HSO_4)_2$
B) Silver peroxide, Ag_2O_2
C) Dialuminum trioxide, Al_2O_3
D) Phosphorus sulfide, P_2S_3
E) Ammonium bicarbonate, NH_3HCO_3

(c) Which of the following combinations of aqueous solutions would result in no reaction?

A) sodium sulfide + calcium nitrate
B) lithium sulfate + barium acetate
C) silver nitrate + sodium phosphate
D) barium chloride + lead acetate
E) zinc nitrate + lithium hydroxide

(d) Which of the following is true of an unsaturated solution?

A) $Q > K_{sp}$
B) $Q < K_{sp}$
C) $Q = K_{sp}$
D) $Q = K_{sp}^{-1}$
E) $Q = K_{sp}^{2}$

(e) Which among the following choices is most likely to be oxidized?

A) Cu (s)
B) Li (s)
C) Zn (s)
D) Ag (s)
E) Fe (s)

(f) In a galvanic cell setup for the reaction $Cr\,(s) + 3\,Ag^{+}\,(aq) \rightleftharpoons Cr^{3+}\,(aq) + 3\,Ag\,(s)$, the overall cell potential will be less than the expected value under standard conditions if:

A) The salt bridge is made narrower.
B) The concentration of Ag^{+} is made larger.
C) The concentration of Cr^{3+} is made larger.
D) The silver electrode is made larger.
E) The chromium electrode is made larger.

(g) Which lattice structure is not based on the closed pack arrangement of anions:

A) CsCl B) ZnS (blende) C) LiCl D) CaF_2

(h) Which is the most likely to adopt a square planar coordination:

A) $[AuCl_4]^-$ B) $[Fe(CN)_4]^{2-}$ C) $[NiCl_4]^{2-}$ D) $[Fe(H_2O)_4]^{3+}$

2. Write the correct name for each of the following compounds.

(a) $Sr(ClO_4)_2$ Strontium Perchlorate (c) P_2S_3 Diphosphorus trisulfide

(b) Co_3N_2 Cobalt (II) nitride (d) $Ni(C_2H_3O_2)_2$ Nickel (II) acetate

3. Consider crystal Ge.

(a) Assuming that Ge assumes a structure similar to sphalerite, describe its structure in terms of close-packing.

Zn S cubic. FCC Ge with Ge in ½ T_d sites.

(b) Given that the density of Ge is 5.323 g/cm^3, determine the Ge-Ge bond length.

Ge - Ge is corner to T_d site

$\Rightarrow \frac{1}{4}$ diagonal $\Rightarrow \frac{\sqrt{3}}{4}a$

$$\rho = \frac{MW \cdot Z}{N_A \cdot a^3} \Rightarrow a = \left[\frac{(72.59)(8)}{(6.022\times10^{23})(5.323)}\right]^{1/3}$$

$$a = 5.66\,\text{Å}$$

$$R(\text{Ge-Ge}) = \frac{\sqrt{3}}{4}a = 2.45\,\text{Å}$$

4. Answer the following questions about the element tellurium, Te.

(a) Samples of natural tellurium contain eight different stable isotopes of the element. In terms of atomic structure, explain what these isotopes have in common and how they differ.

In common, same # of protons

Differ: # of neutrons (also mass number).

(b) Would you expect an object made of pure tellurium to be magnetic? Why or why not?

Yes Te has 2 unpaired e^- in 5p orbitals

(c) Write a balanced nuclear reaction that represents that most likely first *natural* decay pathway for a nuclide of Te-120.

Te-120 neutron poor ⇒ e^- capture

$$^{120}_{52}\mathrm{Te} + {}^{0}_{-1}e \longrightarrow {}^{120}_{51}\mathrm{Sb}$$

(d) How would you expect the electron affinity of tellurium to compare with that of sulfur and with that of xenon? Explain your comparisons.

Te < S for EA since larger ⇒ better shielding than S.

Te > Xe since noble gases are unreactive.

5. Consider the following redox reaction:

$$\overset{+1\ -2}{4\,H_2O\,(l)} + \overset{+7\ -2}{2\,MnO_4^-\,(aq)} + \overset{+3\ -2}{3\,C_2O_4^{2-}\,(aq)} \longrightarrow \overset{+4\ -2}{2\,MnO_2\,(s)} + \overset{+4\ -2}{6\,CO_2\,(g)} + \overset{-2\ +1}{8\,OH^-\,(aq)}$$

(a) In the spaces above the reaction, assign proper *per atom* oxidation numbers to each atom.

(b) In this reaction, which type of atom is being reduced?

Mn

(c) In this reaction, which ion, compound, or species is the reducing agent?

$C_2O_4^{2-}$

(d) Briefly explain what happens at the atomic level in this reaction that makes it a redox reaction.

Redox reactions are electron transfer processes.

In this reaction carbon atoms are giving Mn electrons.

6. How many grams of $Pb(NO_3)_2$ could you add to a 120 mL solution before any precipitate forms if that solution already contains 2.0×10^{-3} M NaCl and 5.0×10^{-4} M $PbCl_2$? (Assume no volume change upon the addition of solid.)

Initial $[Cl^-] = \frac{2.4 \times 10^{-4} + 1.2 \times 10^{-4}}{.12\ L} = 0.003\ M$

$PbCl_{2(s)} \rightarrow Pb^{2+}_{(aq)} + 2Cl^-_{(aq)}$

$K_{sp} = 1.17 \times 10^{-5} = [Pb][Cl]^2 = (5.00 \times 10^{-4} + x)(0.003)^2$

$x = 1.2995\ M$

$1.2995\ M \times 0.12L \times 331.2g = \boxed{51.6g\ Pb(NO_3)_2.}$

7. The rate constant for the first-order decomposition of the reaction below is $7.48 \times 10^{-3}\ s^{-1}$ at a given temperature. How long (in seconds) will it take for the *total* pressure in the system to rise to 0.200 atm if the initial system contains only 0.100 atm of N_2O_5 (g)?

$$N_2O_5\,(g) \rightleftharpoons 2\,NO_2\,(g) + \frac{1}{2}\,O_2\,(g)$$

.100 atm	0	0
$-x$	$+2x$	$+\frac{1}{2}x$
$0.100 - x$	$2x$	$\frac{x}{2}$

$(0.100 - x) + 2x + \frac{x}{2} = 0.200$ atm

$\Rightarrow x = 0.067$ atm.

$[N_2O_5]_f = 0.100 - x = 0.033$ atm

1st order $\Rightarrow \ln[A](t) = -kt + \ln[A]_0$

$\ln(0.033) = -7.48 \times 10^{-3} t + \ln 0.100$

$\boxed{t = 148\ s}$

8. Consider the following questions related to this redox reaction at 298K.

$$MnO_2\,(s) + Al\,(s) \longrightarrow Mn^{2+}\,(aq) + Al^{3+}\,(aq)$$

(a) Balance the above redox reaction, assuming an acidic solution.

$12H^+_{(aq)} + 3MnO_{2(s)} + 2Al_{(s)} \rightarrow 3Mn^{2+}_{(aq)} + 6H_2O_{(l)} + 3Al^{3+}_{(aq)}$

(b) The reaction above initially contains 10.0 g $Al(NO_3)_3\,(aq)$ and excess $MnO_2\,(s)$ in a total volume of 2.2 L at an initial pH of 1.2. Once the reaction has reached equilibrium the $[Mn^{2+}]$ is 0.0012 M. Calculate the overall cell potential for this reaction under these conditions.

$[H^+]_i = 10^{-pH} = 0.063\ M$

$[Al^{3+}]_i = 10.0\,g \times \frac{1\,mol}{212.98\,g} \times \frac{1\,mol}{1\,mol} \frac{1}{2.2\,L} = 0.0213\ M$

	$12H^+$	+ $3MnO_2$	+ $2Al$	$\rightarrow$ $3Mn^{2+}$	+ $6H_2O_{(l)}$	+ $3Al^{3+}$
	0.063	—	—	0	—	0.0213
	$-12x$	—	—	$+3x$	—	$+2x$
	$0.063-12x$	—	—	$3x$	—	$0.0213+2x$

$3x = 0.0012 \Rightarrow x = 0.0004\ M$

$E^\circ = E^\circ_{cat} - E^\circ_{an} = 1.21\ V - (-1.66V) = 2.87\ V$

$E = E^\circ - \frac{0.0592}{n} \log Q = 2.87V - \frac{0.0592\ V}{6\,mol} \log\left[\frac{(0.0012)^3(0.0221)^2}{(0.0582)^{12}}\right]$

$= \boxed{2.84\ V}$

9. (a) An electrolytic cell has an iron anode in a solution of iron (III) nitrate. How must you construct the other half cell if the overall voltage required to power the cell is -0.094 V under standard conditions?

Anode: $Fe(s) \rightarrow Fe^{3+}_{(aq)} + 3e^-$ $E^\circ = 0.036\,V$

Cathode: ? $E^\circ = ?$

$E^\circ_{cell} = -0.094\,V$

$x = -0.13\,V \Rightarrow \boxed{Pb^{2+}|Pb}$

(b) You decide to use a Cu/Cu^{2+} concentration cell as a battery to power the reaction in part (a). The cathode half-cell has been set up for you and is composed of a solid piece of copper in 5.0 M $Cu(NO_3)_2$ (aq). How many grams of $Cu(NO_3)_2$ must be added to 0.75 L of water in the other half-cell to produce a sufficient overall voltage to power the reaction in part (a)? Cathode more concentrated.

$$E = E^\circ - \frac{0.0592\,V}{n}\log Q = 0.094\,V = 0 - \frac{0.059\,V}{2}\log\left(\frac{x}{5.0\,M}\right)$$

$x = 0.0033\,M\ Cu(NO_3)_2$

$0.0033\,M \times 0.75\,L = 0.0025\,mol\ Cu(NO_3)_2 \times \frac{187.55\,g}{mol}$

$= \boxed{0.47\,g\ Cu(NO_3)_2}$

10. Your special someone has requested a ring made purely of rhodium, but rhodium is expensive and you're on a budget. Being a crafty chemist, you decide to use a plating cell to plate a cheap silver ring with rhodium (No one will notice the difference right?). Your special someone is coming over yo your place in exactly 2 hours. If you start right now, will you have enough time to plate 7.0 g of rhodium onto the ring using a current of 2.3 A in your plating cell?

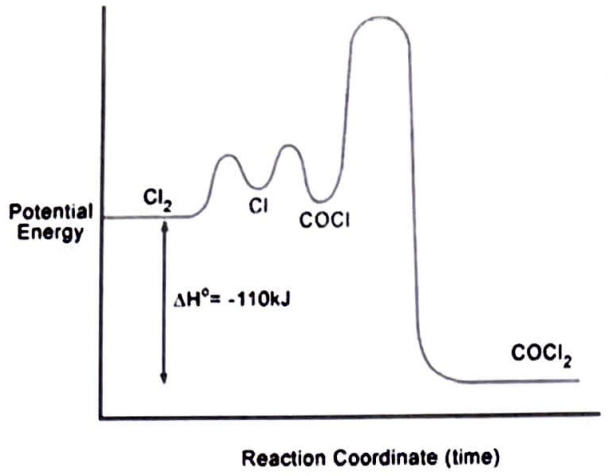
$$Rh^{3+}(aq) + 3e^- \longrightarrow Rh(s)$$

$$7.0\,g \times \frac{1\,mol}{102.9\,g} \times \frac{3\,mole^-}{1\,mol} \times \frac{96,485\,C}{mole^-} \times \frac{1\,sec}{2.3\,C} \times \frac{1\,hr}{3600\,s} = 2.38\,hr$$

$\boxed{No}$ not enough time.

They will be quite disappointed.

11. Given the following mechanism and energy diagram, determine the **rate** for the overall reaction if you start with 0.25 M CO and 0.30 M Cl_2 ($k_{overall} = 11\ M^{-3/2}s^{-1}$).



Overall Reaction:

$$CO\,(g) + 2\,Cl_2\,(g) \longrightarrow COCl_2\,(g) + 2\,Cl\,(g)$$

Proposed Mechanism:

$$Cl_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,Cl\,(g)$$

$$Cl\,(g) + CO\,(g) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CoCl\,(g)$$

$$Cl_2\,(g) + COCl\,(g) \xrightarrow{k_3} COCl_2\,(g) + Cl\,(g)$$

3rd step is slowest.

rate = $k_3[Cl_2][COCl]$

~~$k_2[Cl][CO] = k_{-2}$~~ $k_2[Cl][CO] = k_{-2}[COCl]$

$[COCl] = \frac{k_2}{k_{-2}}[Cl][CO]$

rate = $\frac{k_3 k_2}{k_{-2}}[Cl_2][Cl][CO]$

$k_1[Cl_2] = k_{-1}[Cl]^2 \qquad [Cl] = \left(\frac{k_1}{k_{-1}}\right)^{1/2}[Cl_2]^{1/2}$

rate = $k_3 \frac{k_2}{k_{-2}}\left(\frac{k_1}{k_{-1}}\right)^{1/2}[Cl_2]^{3/2}[CO] = k_{ov}[Cl_2]^{3/2}[CO]$

rate = $\left(11\ \frac{M^{-3/2}}{s}\right)(0.30M)^{3/2}(0.25M)$

= $\boxed{0.45\ M/s}$

12. A student investigated the reaction **heat + A + B + 2C** $\longrightarrow$ **D** for 200 seconds per trial at 25°C, with the data collected shown in the table provided on the right.

Trial	$[A]_i$ (M)	$[B]_i$ (M)	$[C]_i$ (M)	Initial Rate (M/s)
1	0.30	0.05	0.05	6.0×10^{-5}
2	0.30	0.10	0.05	6.0×10^{-5}
3	0.40	0.05	0.20	3.2×10^{-4}
4	0.40	0.05	0.05	8.0×10^{-5}

Given this information, along with the fact that the activation energy for the slowest step of this reaction's mechanism is 40 kJ/mol, calculate the initial rate for this reaction it it were run at 40°C using the same initial concentrations as in trial 3.

rate $= k A^x B^y C^z$

Trial 1 & 4 $\Rightarrow$ Δrate $= \Delta$Conc^x $\Rightarrow$ $1.33 = 1.33^x$ $\quad x = 1$

Trial 1 & 2 $\Rightarrow$ Δrate $= \Delta$Conc^y $= 1 = 2^y$ $\quad y = 0$

Trial 3 & 4 $\Rightarrow$ Δrate $= \Delta$Conc^z $\Rightarrow$ $4 = 4^z$ $\Rightarrow$ $z = 1$

rate $= k[A][C]$

Solve for k at 40°C.

$$\ln\left(\frac{k_2}{0.004}\right) = \left(\frac{-40{,}000\ \text{J/mol}}{8.314\ \text{J/mol K}}\right)\left(\frac{1}{313\text{K}} - \frac{1}{298\text{K}}\right)$$

$k_2 = 0.00867\ M^{-1}s^{-1}$ at 40°C

rate $= (0.00867\ M^{-1}s^{-1})(0.40)(0.20)M^2$

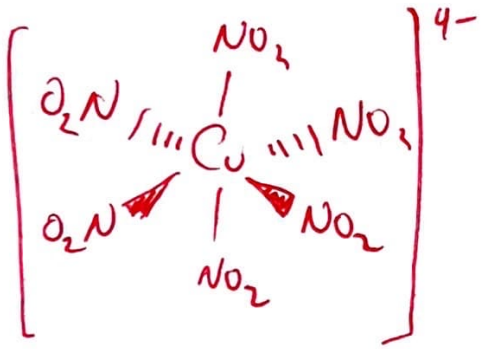
$= 6.94 \times 10^{-4}\ \frac{M}{s}$

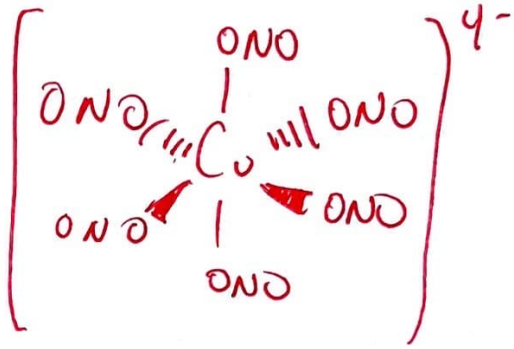
13. Consider the structure of hexanitrocuprate (II).

(a) What is the chemical formula for this structure?

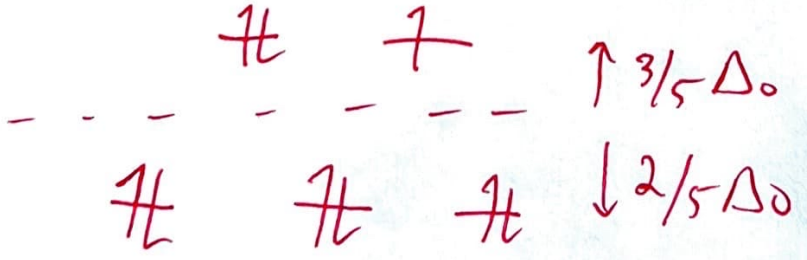
$[Cu(NO_2)_6]^{4-}$

(b) Draw all linkerage isomers.





(c) Assuming that the crystal field is the same in both isomers, draw the crystal field diagram and give the CFSE. Cu^{2+} is d^9



$6\left(-\frac{2}{5}\Delta_o\right) + 3\left(\frac{3}{5}\Delta_o\right) = -\frac{12}{5}\Delta_o + \frac{9}{5}\Delta_o = \boxed{-\frac{3}{5}\Delta_o}$

If we include pairing energy:

$\boxed{-\frac{3}{5}\Delta_o + 4P}$

14. Answer the following questions using the picture below of a salt of Buckminsterfullerene (C_{60}, soccer ball) that contains potassium (black spheres).

(a) Describe the structure and determine the number of atoms in the unit cell. C_{60} in FCC with K^+ in all Td : O_h sites

12 K : 240 C ⇒ 252 atoms

(b) What is the mass of a single unit cell?

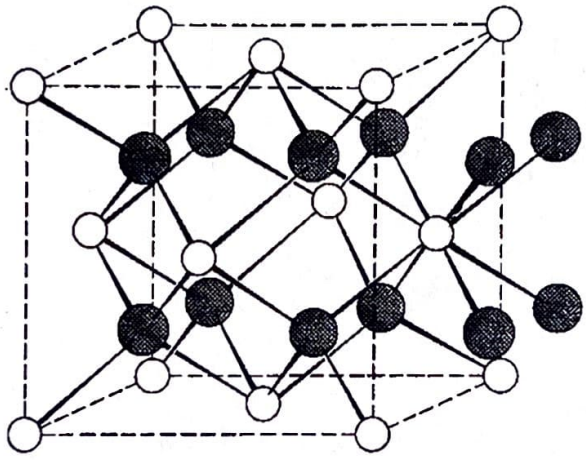
(12)(39.0983 u) + (240)(12.011 u)

= 3351.81 u

(c) Explain what would happen if Rubidium is substituted for potassium to the lattice parameter.

Rubidium is larger ⇒ lattice parameter will increase.

15. The unit cell shown below is for a compound Ba_xI_y.



(a) Determine the chemical formula (ie the lowest whole number values for x and y).

BaI_2

(b) How many Ba ions, I ions, and formula units are in this unit cell?

4 formula units

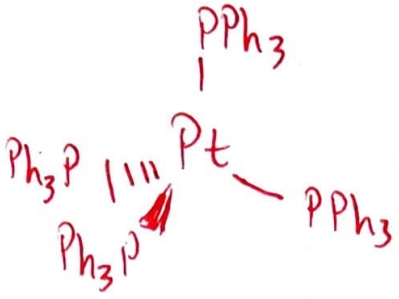
(c) Describe the placement of Ba ions and I ions.

Ba in FCC lattice ; I in all T_d sites.

16. Determine the structure and magnetic properties of the following compounds.

(a) $Pt(P(CH_3)_3)_4$

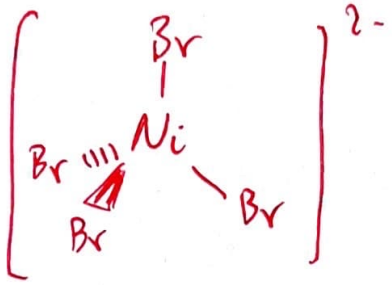
T_d, d^{10}



Diamagnetic

(b) $[NiBr_4]^{2-}$

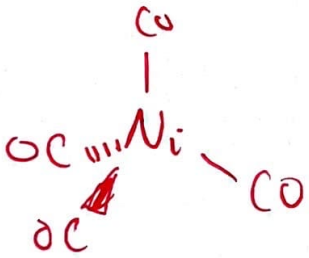
T_d, d^8 hs.



Paramagnetic

(c) $Ni(CO)_4$

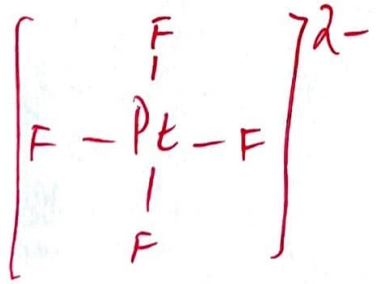
T_d, d^{10}



Diamagnetic

(d) $[PtF_4]^{2-}$

Sq. Planar
d^8, hs.



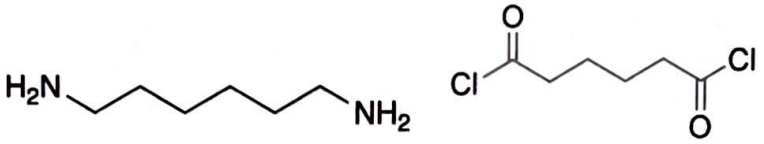
Diamagnetic.

(e) Which of the above four complexes is most likely to appear green? Please explain why.

Green ⇒ absorbs red ⇒ weak-field ligand

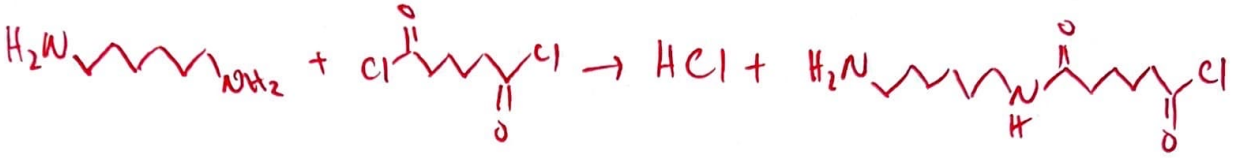
⇒ $NiBr_4^{2-}$

17. In lecture, 6,6 nylon was shown to be produced using hexamethylenediamine and adipic acid. However, in practice 6,6 nylon is made via polymerization of hexamethylenediamine (left) and adipoyl chloride (right) since adipoyl chloride is more reactive. That is, the polymerization will occur more rapidly and at lower temperatures.

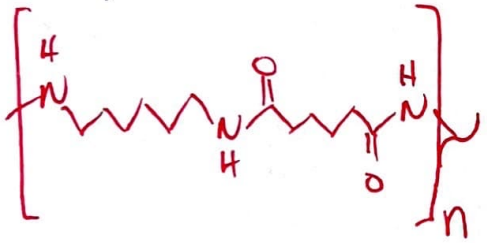


(a) What type of polymerization will occur? Condensation

(b) What are the products if 1 hexamethylenediamine and 1 adipoyl chloride react?

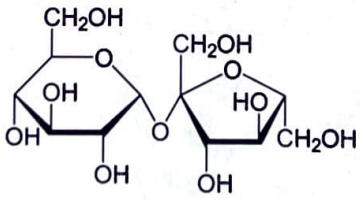


(c) Draw the repeat unit that results from the polymerization of adipoyl chloride and hexamethylenediamine.



6.6 nylon from lecture.

18. Sucrose, ie table sugar, shown below is made up of a molecule of glucose (left) and fructose (right).



(a) What type of bond connects fructose and glucose? glycosidic linkage

(b) What type of carbohydrate is fructose? monosaccharide

(c) What type of carbohydrate is glucose? monosaccharide

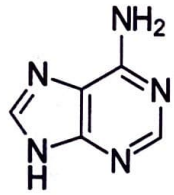
(d) What type of carbohydrate is sucrose? disaccharide.

19. What is the currently accepted hypothesis for why proteins fold?

Entropy driven by the hydrophobic effect.

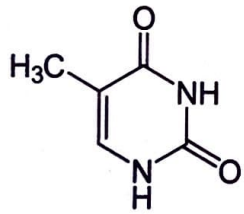
Water entropy increased, force a hydrophobic core to form and place hydrophilic residues on the surface.

20. Lets consider some of the building blocks of life. For each of the following molecules, determine if they will rotate plane-polarized light or not.



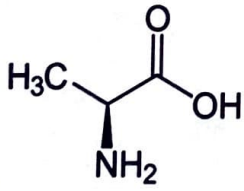
(a) Adenine

No, achiral



(b) Thymine

No, achiral



(c) Alanine

Yes, this is chiral

If you recall, alanine is an amino acid, and in general the left most methyl group is replaced by other substituents to form other types of amino acids. It should hence be noted that nature has a preferred handedness and it is not exactly known why. For example, the DNA helix is a right-handed helix whereas amino acids are left-handed, despite left-handed helix's and right-handed amino acids being possible to make.

Good Luck!