

Name _____ KEY _____

Please show your work for partial credit.

You may not use notes or other materials with chemical information without the instructor's approval; necessary information is provided on pages at the back of the exam. Please do not use ipods or other music players.

hydrogen 1 H 1.0079																	helium 2 He 4.0026	
lithium 3 Li 6.941	beryllium 4 Be 9.0122											boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180	
sodium 11 Na 22.990	magnesium 12 Mg 24.305											aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948	
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80	
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29	
cesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-102 * *	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	unnilium 110 Uu [271]	ununium 111 Uuu [272]	unbibium 112 Uub [277]	ununquadium 114 Uuq [289]					

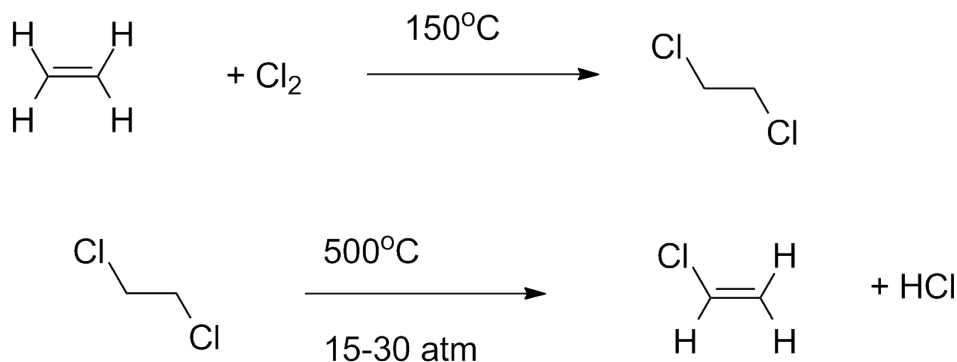
* Lanthanide series

lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendeleevium 101 Md [258]	nobelium 102 No [259]

** Actinide series

1. (30 points) Poly(vinylchloride) is a polymer made from a free radical reaction of chloroethene (also called vinyl chloride).

A. Vinyl chloride is made in two steps in the gas phase:



Calculate the equilibrium constant for each step of the reaction at the temperature indicated.

Step 1.

$$\begin{aligned}
 \Delta H^\circ_r &= -132.0 \text{ kJ/mol} - (52.4 \text{ kJ/mol} + 0) = -184.4 \text{ kJ/mol} \\
 \Delta S^\circ_r &= 303.5 \text{ J/(mol-K)} - \{219.3 \text{ kJ/(mol-K)} + 223.1 \text{ kJ/(mol-K)}\} = -138.9 \text{ J/(mol-K)} \\
 \Delta G^\circ_r &= \Delta H^\circ_r - T\Delta S^\circ_r = -186400 \text{ J/mol} - 423\text{K}\{-138.9 \text{ J/(mol-K)}\} = -125.6 \text{ kJ/mol} \\
 \Delta G^\circ_r &= -RT \ln K_{\text{eq}}, \text{ so } K_{\text{eq}} = e^{+35.7} = 3.24 \times 10^{15}
 \end{aligned}$$

(ΔG°_r is large and negative; K_{eq} is therefore large.)

Step 2.

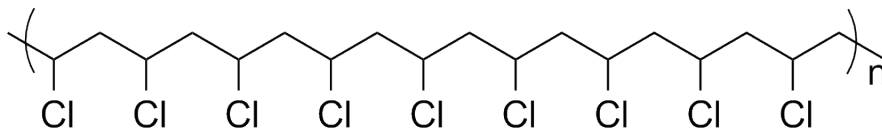
$$\begin{aligned}
 \Delta H^\circ_r &= (-92.31 \text{ kJ/mol} + 22.0 \text{ kJ/mol}) - \{-132.0 \text{ kJ/mol}\} = +61.7 \text{ kJ/mol} \\
 \Delta S^\circ_r &= \{189.6 \text{ J/(mol-K)} + 264.0 \text{ kJ/(mol-K)}\} - 303.5 \text{ J/(mol-K)} = +147.4 \text{ J/(mol-K)} \\
 \Delta G^\circ_r &= \Delta H^\circ_r - T\Delta S^\circ_r = 61700 \text{ J/mol} - 773\text{K}\{147.4 \text{ J/(mol-K)}\} = -52.3 \text{ kJ/mol} \\
 \Delta G^\circ_r &= -RT \ln K_{\text{eq}}, \text{ so } K_{\text{eq}} = e^{+8.14} = 3422
 \end{aligned}$$

B. Explain how ΔS°_r for each reaction says whether we need to run the reaction at as high a temperature as practical, or as low a temperature as possible.

For step 1, ΔS°_r is negative. As temperature rises, $T \Delta S^\circ_r$ becomes more positive, disfavoring the reaction. This is balanced by a very negative ΔH°_r ; practically it does not matter, but as a general rule we want to run the reaction at the lowest temperature possible.

For step 2, the signs on ΔH°_r and ΔS°_r are both positive. For the reaction to be favored, ΔG°_r must be negative, so we need entropy to dominate and therefore a high reaction temperature is mandatory.

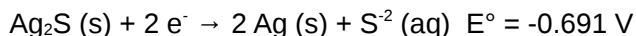
C. The polymer structure is shown below.



One concern with this polymer is that, during a fire, it can emit HCl. Describe the chemical origin of this and predict whether this is always a risk during thermal decomposition, or if there is a temperature at which it starts to be a problem.

This is an elimination reaction that creates double bonds along the chain. It looks a lot like the second step in the vinyl chloride synthesis, so we expect that there will be some temperature at which $\Delta H_r^\circ = T \Delta S_r^\circ$. We would need more information about the thermodynamic properties of the polymer to determine what temperature that is; the entropy of the polymer in particular will be much different.

2. (40 points) One of the major components of silver tarnish is silver sulfide, Ag_2S . Other than abrasion (undesirable because of the removal of silver), the main function of most silver cleaners is to reduce the silver sulfide to silver metal. The half cell reaction is:



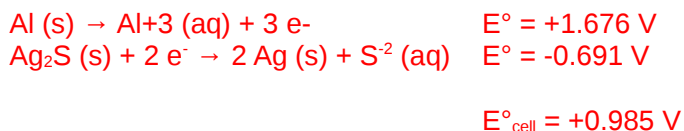
One approach is as follows:

A tarnished silver spoon is placed in direct contact with a commercially available metallic product in a glass baking dish. Boiling water, to which some baking soda (NaHCO_3) has been added, is poured into the dish to completely cover the spoon and the metal object. Within a short time, the tarnish is removed as the silver sulfide is reduced to silver.

A. Based on the electrochemical tables provided, what metal or metals might be present in the metallic object?

The oxidation potential must be $>+0.691 \text{ V}$ for reduction of silver sulfide to occur. Aluminum, zinc and magnesium are the most practical candidates; Na, K, Li and Ca all fit the electrochemical restriction but are too reactive with water to work well. (Even Mg is a concern.)

B. For one of these (the one you'd select if you were in charge), write the half cell reaction for oxidation, and demonstrate that the overall process is thermodynamically favorable.



C. Why is NaHCO_3 added?

If there is too much $[\text{H}_3\text{O}^+]$, the electropositive metal will reduce protons to H_2 . NaHCO_3 acts as a base to suppress that.

D. One of these metal objects has been marketed for \$50, making several claims:

- You more than pay for the object in the value of the recovered silver;
- It avoids using any chemicals;
- The product will never need to be replaced.

Explain whether you believe the claims (and why), and whether you would think this is a good deal that justifies the expense (assuming you have a fair amount of silver that regularly needs cleaning).

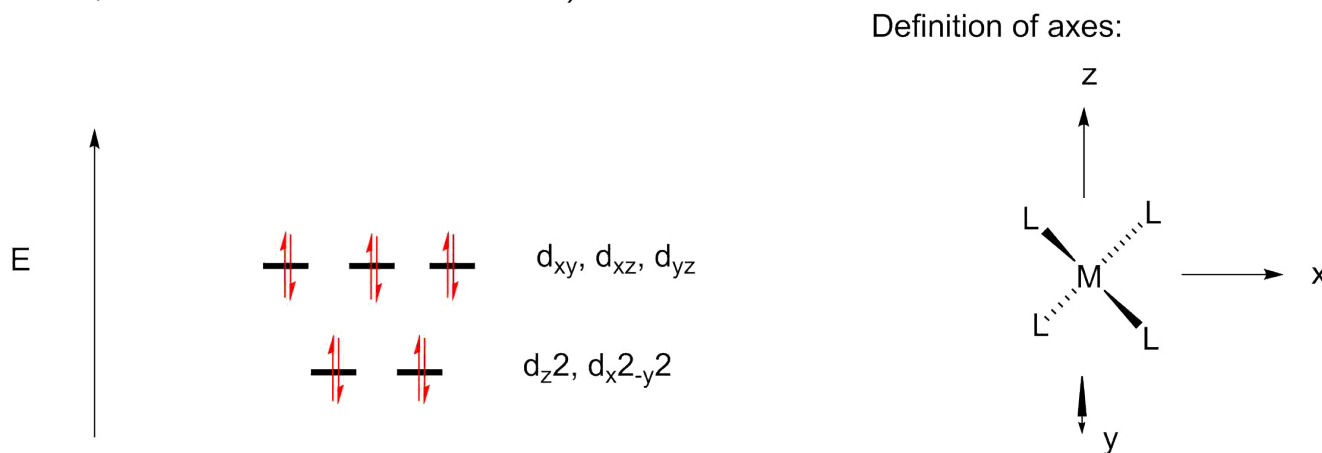
We'll accept pretty much anything that you say that illustrates how you incorporate the chemistry into your judgment. My judgment is that the claims are generally bogus:

- a 2-cent piece of aluminum foil works as effectively;
- This is a chemical process (though largely benign);
- Practically never needing replaced? Yes. However, you are consuming the aluminum (or other electropositive metal) in proportion to the silver sulfide reduced.

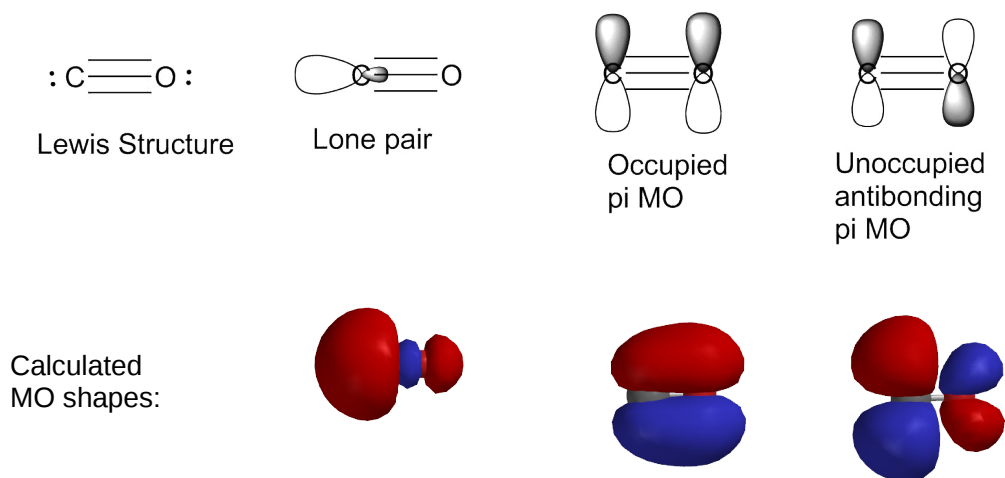
3. (40 points) Nickel mining and refining involves reversible formation of nickel carbonyl, using carbon monoxide. The raw ore (a combined mixture of iron and nickel sulfides) is reduced to a mixture of iron and nickel metals, then CO is used to convert the nickel to nickel carbonyl, a liquid compound that can be distilled away from the iron. Once separated, nickel carbonyl can then be heated to a higher temperature, causing thermal decomposition to the free metal.



A. This metal complex is tetrahedral. The d-orbital energy level diagram for a tetrahedral complex is shown below. Show where the valence electrons are. (Two hints: nickel in this complex is considered to be in the 0 oxidation state; in compounds like this, the 3d orbitals are all lower in energy than the 4s or 4p orbitals, which is not the case for a free atom.)



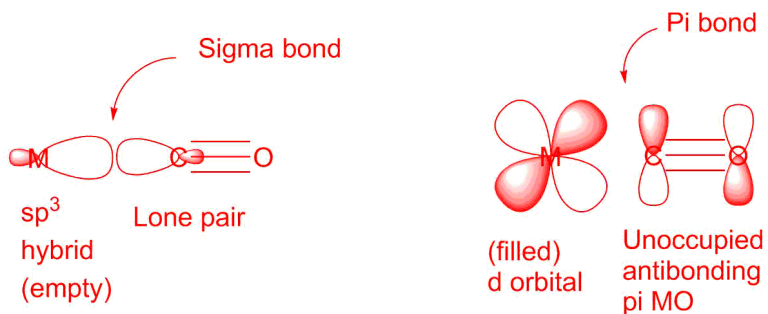
B. Metal carbonyl complexes exhibit two kinds of bonding to the d orbitals. Two important orbitals for CO are shown below; describe (using words and pictures) how each forms a new MO when bonding to the metal orbital (d or sp^3 hybrid). Be sure to factor in which orbitals are filled and which are empty. (Use the back of the page if you need space.)



Two major interactions are at play.

1. The CO lone pair needs to interact with an empty orbital at the metal: an sp^3 hybrid (for a tetrahedral metal) works. This forms a sigma bond.

2. There is a “backbonding” interaction between metal d orbitals (full) and the empty antibonding pi orbital of CO. This forms a pi bond.



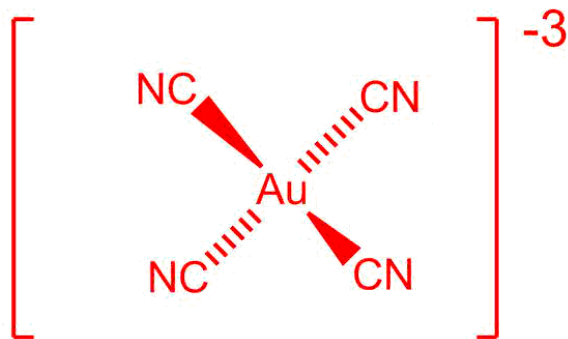
Note that since the pi orbital of CO is full, there is no empty orbital on the metal with which it can form a net bonding interaction.

C. Gold refining involves creating a similar complex between Au(I) and cyanide (CN⁻). Describe how the MOs in cyanide are similar to those in carbon monoxide.

Cyanide is isoelectronic with CO, and although the precise energy levels will change, the overall bonding picture between CN⁻ and a metal is identical to that between CO and a metal.

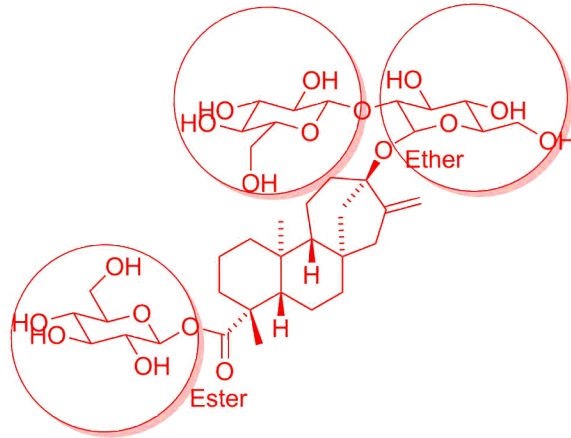
(Note also that Au(I) will have a similar d¹⁰ electron configuration.)

D. Draw the structure (including net charge) of the gold-cyanide complex ion you expect to form in the gold refining process.



(tetrahedral, 4-coordinate, net charge -3)

4. (30 points) The structure of a compound from stevia is shown below. This is many hundreds of times sweeter than sucrose, and as such it is used as a naturally occurring low-calorie alternative to sugar.

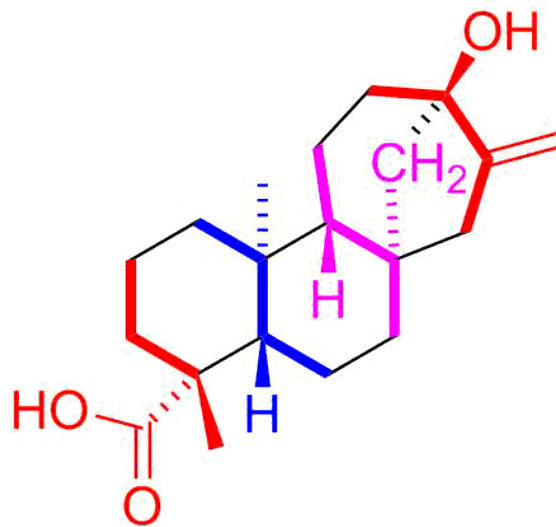


A. Circle the glucose residues.

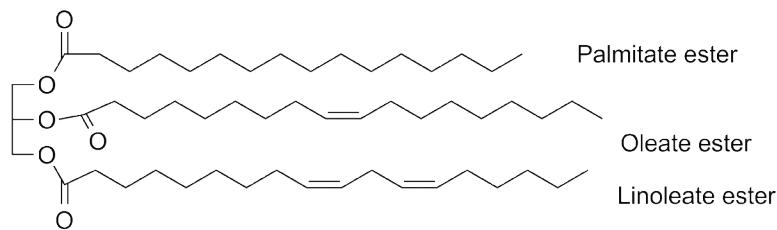
B. Describe the functional group(s) that link the saccharides to the core of the molecule.

One is an ether linkage (formally an acetal); the other is an ester. (Two of the glucoses are linked by an ether/acetal link.)

C. The core is a terpenoid molecule; in the structure below, trace out the isoprene units.



5. (30 points) As we discussed during demonstrations, the product Crisco® was invented as a substitute for animal fats, and was initially prepared from cottonseed oil. Saponification of cottonseed oil gives 54% linoleic acid, 22% palmitic acid, and 19% oleic acid along with other minor components. A triglyceride of these three fatty acids is shown here:



A. Name the major physical difference between animal fats and vegetable oils that Crisco® and similar products attempt to mimic.

Animal fats are generally solid at room temperature; the saturated chains pack efficiently. Vegetable oils are usually liquids at room temperature (or below).

B. What kind of chemical reaction is used to make this product?

Hydrogenation: addition of H_2 across the $C=C$ double bond.

C. Through the years, the vegetable oil used in this process has changed based on a combination of nutritional and health concerns coupled with fluctuation in commodity prices. Since 2004, Crisco® has been made from palm oil, which upon saponification gives 45% palmitic acid, 40% oleic acid and 10% linoleic acid. Aside from the influence of minor components (which may in fact be significant), would you expect the change in the source material to significantly change the product? Explain your reasoning

Generally, no; the object is to hydrogenate the alkene bonds as completely as possible. The actual difference will be the small degree to which this is not accomplished, as well as the degree to which any remaining alkene bonds are isomerized from cis to trans.

6. (30 points) A small protein LysM (48 amino acids) was isolated from E coli and characterized by X-ray crystallography. This turns out to be a common domain in bacterial proteins that is used for molecular recognition of oligopeptides and peptidoglycans.

The primary structure is

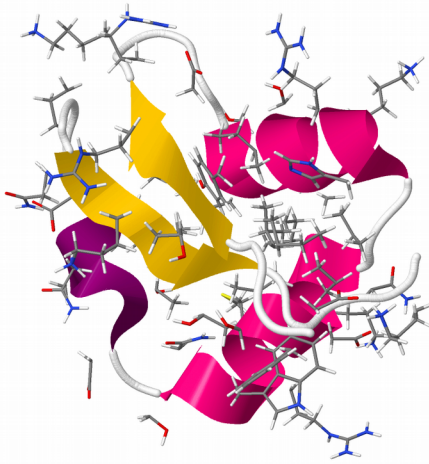
ASP	SER	ILE	THR	TYR	ARG	VAL	ARG	LYS	GLY	ASP	SER	LEU
SER	SER	ILE	ALA	LYS	ARG	HIS	GLY	VAL	ASN	ILE	LYS	ASP
VAL	MET	ARG	TRP	ASN	SER	ASP	THR	ALA	ASN	LEU	GLN	PRO
GLY	ASP	LYS	LEU	THR	LEU	PHE	VAL	LYS				

A. Identify the amino acid at the N-terminus and that at the C-terminus.

N-terminus: **Aspartic acid**

C-terminus: **Lysine**

B. Examine the illustration of the structure of the protein below. The side chains are the light lines; the peptide backbone is illustrated in “cartoon” fashion.

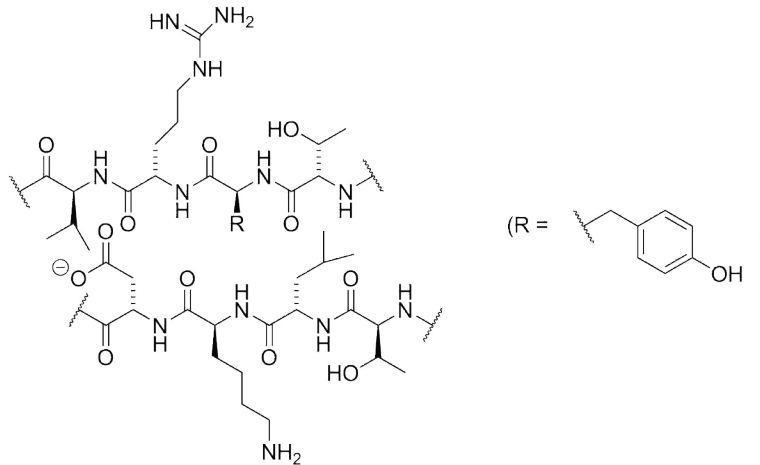


Jmol

Name the two dominant elements of secondary structure this illustrates.

There are α -helices (two of them—the magenta curlicues) and a β -sheet (the yellow arrows).

C. One of these elements of secondary structure is shown below. Circle the hydrogen bonds that hold this piece together.



D. Trypsin is a protease enzyme that cleaves amide linkages containing the carboxyl group of either lysine (LYS) or arginine (ARG). List the fragments that would be formed from trypsin digestion of LysM.

ASP SER ILE THR TYR ARG
 VAL ARG
 LYS
 GLY ASP SER LEU SER SER ILE ALA LYS
 ARG
 HIS GLY VAL ASN ILE LYS
 ASP VAL MET ARG
 TRP ASN SER ASP THR ALA ASN LEU GLN PRO GLY ASP LYS
 LEU THR LEU PHE VAL LYS

Selected data that may be of use:

Physical constants:

$$g = 9.8 \text{ m/s}^2$$

$$\epsilon_0 = 8.85419 \times 10^{-12} \text{ C}^2/(\text{Nm}^2)$$

$$c = 2.99792458 \times 10^{10} \text{ cm/s}$$

$$R = 0.08206 \text{ L-atm}/(\text{mol-K}) = 8.314 \text{ J}/(\text{mol-K})$$

$$N = 6.022 \times 10^{23}$$

$$k = 1.381 \times 10^{-23} \text{ m}^2\text{kg}/(\text{K-s}^2)$$

$$h = 6.626 \times 10^{-34} \text{ m}^2\text{kg/s}$$

$$F = 96485 \text{ C/mol}$$

$$\pi = 3.14159$$

$$e = 2.71828$$

Gravitational Constant
 Electric susceptibility of a vacuum
 Speed of light
 Gas constant
 Avogadro's Number
 Boltzmann constant
 Planck's constant
 Faraday's constant

Properties of State

Species	ΔH_f°	S°
$\text{N}_2(\text{g})$	0 kJ/mol	191.6 J/(mol-K)
$\text{O}_2(\text{g})$	0 kJ/mol	205.1 J/(mol-K)
$\text{Cl}_2(\text{g})$	0 kJ/mol	223.1 J/(mol-K)
$\text{NO}(\text{g})$	90.25 kJ/mol	210.8 J/(mol-K)
$\text{Ag}(\text{s})$	0 kJ/mol	42.55 J/(mol-K)
$\text{Ag}^+(\text{aq})$	105.6 kJ/mol	72.68 J/(mol-K)
$\text{K}^+(\text{aq})$	-254.4 kJ/mol	102.5 J/(mol-K)
$\text{Zn}(\text{s})$	0 kJ/mol	41.63 J/(mol-K)
$\text{Zn}^{2+}(\text{aq})$	-153.9 kJ/mol	112.1 J/(mol-K)
$\text{C}_2\text{H}_4(\text{g})$ (ethylene)	52.4 kJ/mol	219.3 J/(mol-K)
$\text{C}_2\text{H}_4\text{Cl}_2(\text{g})$ (1,2-dichloroethane)	-132.0 kJ/mol	303.5 J/(mol-K)
$\text{C}_2\text{H}_3\text{Cl}(\text{g})$ (chloroethene)	22.0 kJ/mol	264.0 J/(mol-K)
$\text{HCl}(\text{g})$	-92.31 kJ/mol	186.9 J/(mol-K)

Electromotive series:

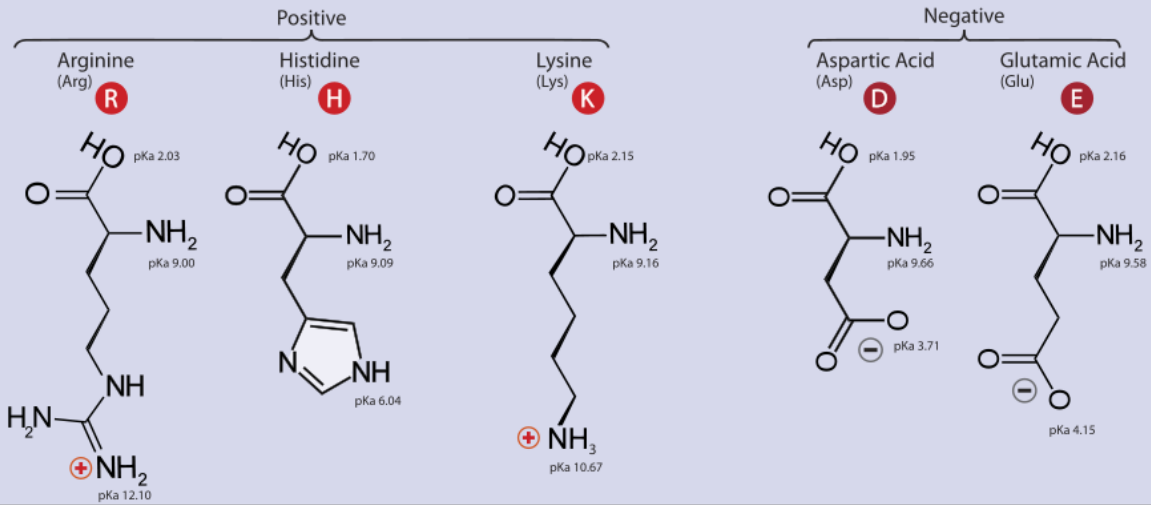
TABLE 20.1 Some Selected Standard Electrode (Reduction) Potentials at 25 °C

Reduction Half-Reaction	E°, V
Acidic solution	
$F_2(g) + 2 e^- \longrightarrow 2 F^-(aq)$	+2.866
$O_3(g) + 2 H^+(aq) + 2 e^- \longrightarrow O_2(g) + H_2O(l)$	+2.075
$S_2O_8^{2-}(aq) + 2 e^- \longrightarrow 2 SO_4^{2-}(aq)$	+2.01
$H_2O_2(aq) + 2 H^+(aq) + 2 e^- \longrightarrow 2 H_2O(l)$	+1.763
$MnO_4^-(aq) + 8 H^+(aq) + 5 e^- \longrightarrow Mn^{2+}(aq) + 4 H_2O(l)$	+1.51
$PbO_2(s) + 4 H^+(aq) + 2 e^- \longrightarrow Pb^{2+}(aq) + 2 H_2O(l)$	+1.455
$Cl_2(g) + 2 e^- \longrightarrow 2 Cl^-(aq)$	+1.358
$Cr_2O_7^{2-}(aq) + 14 H^+(aq) + 6 e^- \longrightarrow 2 Cr^{3+}(aq) + 7 H_2O(l)$	+1.33
$MnO_2(s) + 4 H^+(aq) + 2 e^- \longrightarrow Mn^{2+}(aq) + 2 H_2O(l)$	+1.23
$O_2(g) + 4 H^+(aq) + 4 e^- \longrightarrow 2 H_2O(l)$	+1.229
$2 IO_3^-(aq) + 12 H^+(aq) + 10 e^- \longrightarrow I_2(s) + 6 H_2O(l)$	+1.20
$Br_2(l) + 2 e^- \longrightarrow 2 Br^-(aq)$	+1.065
$NO_3^-(aq) + 4 H^+(aq) + 3 e^- \longrightarrow NO(g) + 2 H_2O(l)$	+0.956
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.800
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.771
$O_2(g) + 2 H^+(aq) + 2 e^- \longrightarrow H_2O_2(aq)$	+0.695
$I_2(s) + 2 e^- \longrightarrow 2 I^-(aq)$	+0.535
$Cu^{2+}(aq) + 2 e^- \longrightarrow Cu(s)$	+0.340
$SO_4^{2-}(aq) + 4 H^+(aq) + 2 e^- \longrightarrow 2 H_2O(l) + SO_2(g)$	+0.17
$Sn^{4+}(aq) + 2 e^- \longrightarrow Sn^{2+}(aq)$	+0.154
$S(s) + 2 H^+(aq) + 2 e^- \longrightarrow H_2S(g)$	+0.14
$2 H^+(aq) + 2 e^- \longrightarrow H_2(g)$	0
$Pb^{2+}(aq) + 2 e^- \longrightarrow Pb(s)$	-0.125
$Sn^{2+}(aq) + 2 e^- \longrightarrow Sn(s)$	-0.137
$Fe^{2+}(aq) + 2 e^- \longrightarrow Fe(s)$	-0.440
$Zn^{2+}(aq) + 2 e^- \longrightarrow Zn(s)$	-0.763
$Al^{3+}(aq) + 3 e^- \longrightarrow Al(s)$	-1.676
$Mg^{2+}(aq) + 2 e^- \longrightarrow Mg(s)$	-2.356
$Na^+(aq) + e^- \longrightarrow Na(s)$	-2.713
$Ca^{2+}(aq) + 2 e^- \longrightarrow Ca(s)$	-2.84
$K^+(aq) + e^- \longrightarrow K(s)$	-2.924
$Li^+(aq) + e^- \longrightarrow Li(s)$	-3.040
Basic solution	
$O_3(g) + H_2O(l) + 2 e^- \longrightarrow O_2(g) + 2 OH^-(aq)$	+1.246
$OCl^-(aq) + H_2O(l) + 2 e^- \longrightarrow Cl^-(aq) + 2 OH^-(aq)$	+0.890
$O_2(g) + 2 H_2O(l) + 4 e^- \longrightarrow 4 OH^-(aq)$	+0.401
$2 H_2O(l) + 2 e^- \longrightarrow H_2(g) + 2 OH^-(aq)$	-0.828

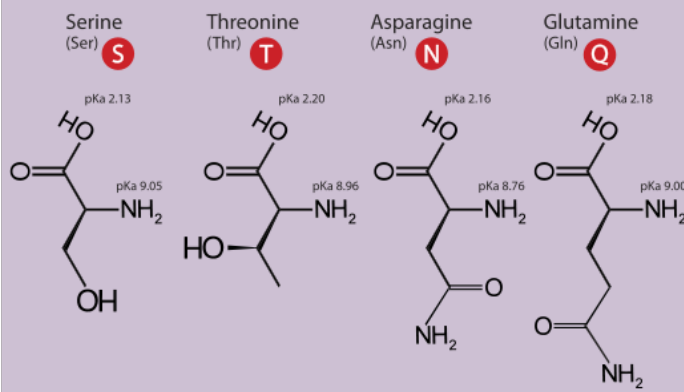
Twenty-One Amino Acids

⊕ Positive ⊖ Negative
• Side chain charge at physiological pH 7.4

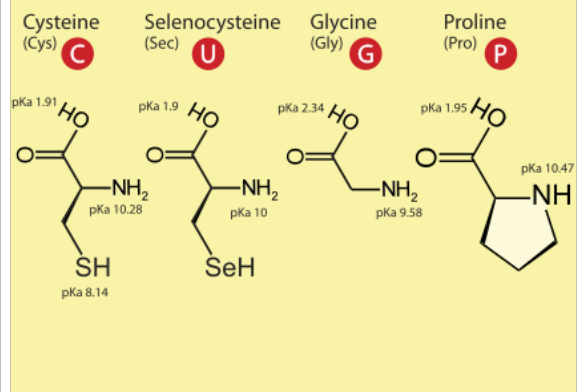
A. Amino Acids with Electrically Charged Side Chains



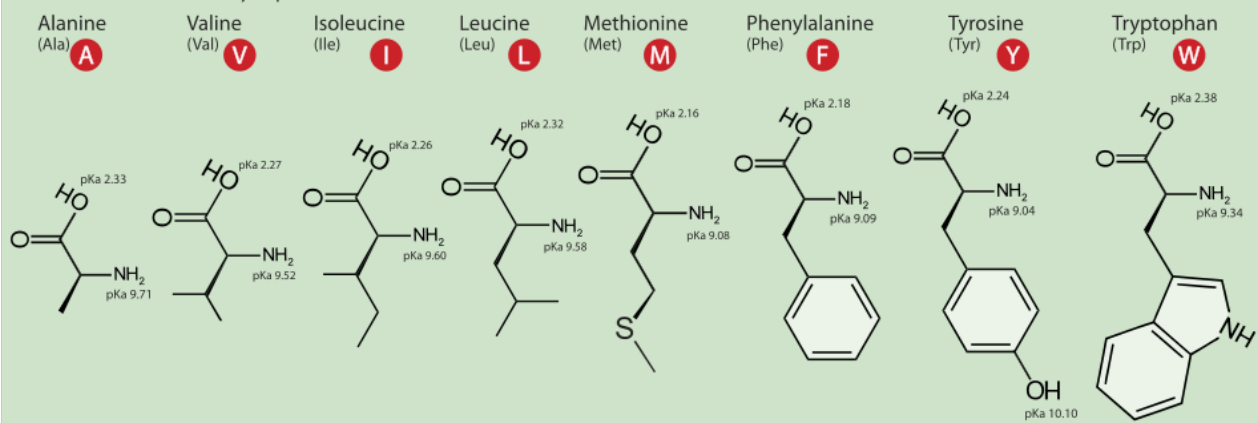
B. Amino Acids with Polar Uncharged Side Chains



C. Special Cases



D. Amino Acids with Hydrophobic Side Chain



pKa Data: CRC Handbook of Chemistry, v. 2010