Problem 1: "A brief history" of life in the universe

1-1. $T = 10^{10} / (1)^{1/2} = 10^{10}$ K (10 billion degrees)

1-2. $T = 10^{10} / (180)^{1/2} = 0.7 \times 10^{9} \approx 10^{9}$ K (1 billion degrees)

1-3 $t = [10^{10}/(3\times10^{3})]^{2}$ s $= 10^{13}$ s $= 3 \times 10^{5}$ yr

1-4. $t = (10^{10}/10^{3})^{2}$ s $= 10^{14}$ s $= 3 \times 10^{6}$ yr

1-5. 100 K

1-6. 10 K

1-7. a - (f) - (d) - (h) - (i) - (c) - (g) - (j) - (e) - (b)

Problem 2: Hydrogen in outer space

2-1. $[(8 \times 8.3 \text{ J K}^{-1} \text{ mol}^{-1} \times 2.7 \text{ K})/(3.14)(10^{-3} \text{ kg mol}^{-1})]^{1/2} = 240 \text{ m s}^{-1}$

2-2. volume of cylinder = $(2)^{1/2}(3.14)(10^{-8} \text{ cm})^{2}(2.4 \times 10^{4} \text{ cm s}^{-1}) = 1.1 \times 10^{-11} \text{ cm}^{3} \text{ s}^{-1}$

2-3. collision/sec = (volume of cylinder) x (atoms/unit volume)

$= (1.1 \times 10^{-11} \text{ cm}^{3} \text{ s}^{-1})(10^{-6} \text{ cm}^{-3}) = 1.1 \times 10^{-17} \text{ s}^{-1}$

time between collisions = $1/(1.1 \times 10^{-17} \text{ s}^{-1}) = 9 \times 10^{16}$ s = about 3 billion yr

2-4. $(240 \text{ m s}^{-1})(9 \times 10^{16} \text{ s}) = 2.2 \times 10^{19}$ m (about 2,000 light yr)

2-5. Speed is proportional to the square root of the temperature.

$(240 \text{ m s}^{-1})(40/2.7)^{1/2} = 920 \text{ m s}^{-1}$

2-6. volume of cylinder = $(2)^{1/2}(3.14)(10^{-8} \text{ cm})^{2}(9.2 \times 10^{4} \text{ cm s}^{-1}) = 4.1 \times 10^{-11} \text{ cm}^{3} \text{ s}^{-1}$

collision/sec = (volume swept per second) x (atoms/unit volume)

$= (4.1 \times 10^{-11} \text{ cm}^{3} \text{ s}^{-1})(1 \text{ cm}^{-3}) = 4.1 \times 10^{-11} \text{ s}^{-1}$

time between collisions = $1/(4.1 \times 10^{-11} \text{ s}^{-1}) = 2.4 \times 10^{10}$ s = about 800 yr

mean free path = $(920 \text{ m s}^{-1})(2.4 \times 10^{10} \text{ s}) = 2.2 \times 10^{13}$ m

λ (intergalactic space)/λ(interstellar space)

$= (2.2 \times 10^{19} \text{ m})/(2.2 \times 10^{13} \text{ m})$ = about a million

2-7. very small

Problem 3: Spectroscopy of interstellar molecules

3-1. $100\lambda = 2.9 \times 10^{-3}$ m K $\qquad\qquad \lambda = 2.9 \times 10^{-5}$ m

E(photon) = hc/λ = $(6.63 \times 10^{-34}$ J s$)$ $(3.0 \times 10^{8}$ m/s$)$ /$(2.9 \times 10^{-5}$ m$)$

= 6.9×10^{-21} J

3-2. J: $0 \leftrightarrow 1$

$\mu = (12\text{x}16/28)(1.66 \times 10^{-27}\text{ kg}) = 1.14 \times 10^{-26}$ kg

$I = \mu R^2 = (1.14 \times 10^{-26}\text{ kg})(1.13 \times 10^{-10}\text{ m})^2 = 1.45 \times 10^{-46}$ kg m^2

$E(0\leftrightarrow1) = 2\, h^2/8\pi^2 I = 2(6.63 \times 10^{-34}\text{ J s})^2/[8\pi^2(1.45 \times 10^{-46}\text{ kg m}^2)]$

$= 7.68 \times 10^{-23}$ J

E(photon) of Problem 3-1 = 6.9×10^{-21} J > $E(0\leftrightarrow1) = 7.68 \times 10^{-23}$ J

Rotational excitation by the background radiation is feasible.

3-3. $E(0\leftrightarrow2) = 6\, h^2/8\pi^2 I = hc/\lambda \qquad\qquad \lambda = 8\pi^2 cI\,/6h$

$I = \mu R^2 = [(1/2) \times 1.66 \times 10^{-27}\text{ kg}](0.74 \times 10^{-10}\text{ m})^2 = 4.55 \times 10^{-48}$ kg m^2

$\lambda = 8\pi^2 Ic\,/6h$

$= [8\pi^2 \times 4.55 \times 10^{-48}\text{ kg m}^2 \times 3 \times 10^{8}\text{ m/s}]/(6 \times 6.63 \times 10^{-34}\text{ J s})$

$= 2.71 \times 10^{-5}$ m

$T = 2.9 \times 10^{-3}$ m K $/\lambda = 2.9 \times 10^{-3}$ m K / 2.71×10^{-5} m = 107 K

Observation of hydrogen rotational spectra is feasible at 100 K.

Problem 4: Ideal gas law at the core of the sun

4-1. protons: (158 g/cm^3 x 0.36)/(1.0 g/mole) = 57 mol/cm^3

helium nuclei: (158 g/cm^3 x 0.64)/(4.0 g/mole) = 25 mol/cm^3

electrons: 57 + (25 x 2) = 107 mol/cm^3

Total: 189 mol/cm^3

4-2. volume of a hydrogen molecule = $2\,(4/3)\,\pi\, r^3$

$= 2 \times (4/3)\,\pi \times (0.53 \times 10^{-8}\text{ cm})^3 = 1.2 \times 10^{-24}$ cm^3

hydrogen gas: $V/n = RT/p$ = (0.082 atm L K^{-1} mol^{-1}) x 300 K / 1 atm

= 24.6 L/mole = 4.1×10^{-23} L/molecule = 4.1×10^{-20} cm^3/molecule

1.2×10^{-24} cm^3 / 4.1×10^{-20} cm^3 = 3×10^{-5} = 0.003 %

liquid hydrogen: (2 g/mole) / (0.09 g/cm^3) / (6×10^{23} molecule /mole)

= 3.7×10^{-23} cm^3

(1.2×10^{-24} cm^3)/(3.7×10^{-23} cm^3) = 0.03 = 3 %

solar plasma: neglect volume of electrons

$(4/3)(\pi)(1.4 \times 10^{-13}\text{ cm})^3\ (1 \times 57\text{ mol/cm}^3 + 4 \times 25\text{ mol/cm}^3)(6 \times 10^{23}\text{ mol}^{-1})$

= 1.1×10^{-12} = 1×10^{-10} %

Volume occupied is extremely small and ideal gas law is applicable.

4-3. From 4-1, we know there are 189 moles of particles/cm^3.

$T = pV/nR$ = $(2.5 \times 10^{11})(1 \times 10^{-3})/(189)(0.082)$ = 1.6×10^7 K

Problem 5: Atmosphere of the planets

5-1. $^{238}_{92}\text{U} \rightarrow\ ^{206}_{82}\text{Pb} + 8\,^{4}_{2}\text{He} + 6\,^{0}_{-1}\text{e}$

5-2. After almost one half-life, the molar ratio between Pb-206 and U-238 is 1.

Mass ratio: Pb-206/U-238 = 206/238 = 0.87

5-3. $(1/2)mv_e^2 = GMm/R$

$v_e^2 = (2GM/R) = [(2)(6.67\times10^{-11}\text{ N m2 kg}^{-2})(5.98 \times 10^{24}\text{ kg})/(6.37 \times 10^6\text{ m})]$

$v_e = 1.12 \times 10^4$ m s^{-1}

5-4. hydrogen atom: $(8RT/\pi M)^{1/2}$

$= [(8)(8.3145\text{ kg m}^2\text{ s}^{-2}\text{ mol}^{-1}\text{ K}^{-1})(298\text{ K})/(3.14)(1.008 \times 10^{-3}\text{ kg mol}^{-1})]^{1/2}$

= 2500 m s^{-1} (22% of the escape velocity)

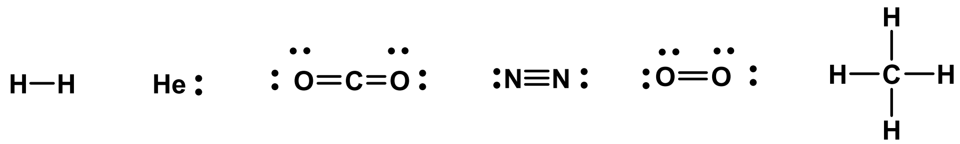
nitrogen molecule:

2500 m s^{-1} x $(1/28)^{1/2}$ = 470 m s^{-1} (4% of the escape velocity)

The fraction with speed exceeding the escape velocity is much greater for hydrogen atoms than for nitrogen molecules.

5-5. a. Jupiter: large mass, low temperature, H/He retained at high pressure
b. Venus: lost light elements, rich in carbon dioxide, high pressure
c. Mars: small mass, rich in carbon dioxide, low pressure
d. Earth: lost light elements, carbon dioxide converted to oxygen through photosynthesis
e. Pluto: very small mass, lost light elements, very low atmospheric pressure

5-6.



5-7. He (4K) < H_2 (20K) < N_2 (77K) < O_2 (90K) < CH_4 (112K)
Dispersion force is greater for larger molecules.
Nitrogen with the triple bond has a smaller bond length than oxygen.
Nitrogen also has less lone pair electrons to be involved in dispersion.

Problem 6: Discovery of the noble gases

6-1. In 1816 Prout published a hypothesis that all matter is composed ultimately of hydrogen. (Later, Harlow Shapley, an eminent astronomer, said that if God did create the world by a word, the word would have been hydrogen.) Prout cited as evidence the fact that the specific gravities of gaseous elements appeared to be whole-number multiples of the value for hydrogen.

6-2. $28\ NH_3 + 21\ O_2 + 78\ N_2 + Ar \rightarrow 92\ N_2 + 42\ H_2O + Ar$

6-3. $[(92)(2)(14.0067) + 39.948]/93 = 28.142$

6-4. $78\ N_2 + 21\ O_2 + Ar + 42\ Cu \rightarrow 78\ N_2 + 42\ CuO + Ar$

6-5. $[(78)(2)(14.0067) + 39.948]/79 = 28.164$

6-6. 28.164/28.142 = 1.0008 (about 0.1%)

6-7. $4\ NH_3 + 3\ O_2 \rightarrow 2\ N_2 + 6\ H_2O$

Molecular weight of pure nitrogen = (2)(14.0067) = 28.013

28.164/28.013 = 1.0054

The discrepancy would increase about 7-fold (0.0054/0.0008).

6-8. 40/29 = 1.4

6-9. $5R/3R = 1.67$ translational

6-10. volume of air = 1000 m^3 = 10^6 liter

$(10^6)/22.4 = 4.5 \times 10^4$ mol of air

weight of argon = $(4.5 \times 10^4)(0.01)(40) = 1.8 \times 10^4$ g = 18 kg

6-11. helium - sun

neon - new

argon - lazy

krypton - hidden

xenon - stranger

Problem 7: Solubility of salts

7-1. $AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq)$

$K_{sp} = [Ag^+][Cl^-] = x^2 = 1.8\times10^{-10} \Rightarrow [Ag^+] = [Cl^-] = 1.3_4\times10^{-5}$ M

$AgBr(s) \rightarrow Ag^+(aq) + Br^-(aq)$

$K_{sp} = [Ag^+][Br^-] = x^2 = 3.3\times10^{-13} \Rightarrow [Ag^+] = [Br^-] = 5.7_4\times10^{-7}$ M

7-2. In this hypothetical case, $[Ag^+] = [Cl^-] = 1.3_4\times10^{-5}$ M just as in 7-1.

$Cl^-(aq)/Cl(total) = Cl^-(aq)/(Cl^-(aq)+AgCl(s))$

$= (1.3\times10^{-5}\ M)(0.200\ L)/1.00\times10^{-4}\ mol = 0.027 = 2.7\%$

7-3. Similarly, $[Ag^+] = [Br^-] = 5.7_4\times10^{-7}$ M just as in 7-1.

$Br^-(aq)$/Br(total) = $Br^-(aq)/(Br^-(aq)$+AgBr(*s*))

= $(5.7\times10^{-7}$ M)(0.200 L)/1.00×10^{-4} mol = 1.1×10^{-3} = 0.11%

7-4. Assume that 1.00×10^{-4} mol of AgCl is precipitated, and 1.00×10^{-6} mol of Ag^+ ion remains in solution. Then a portion of AgCl dissolves.

$[Ag^+] = 5.0\times10^{-6} + x$, $[Cl^-] = x$

$K_{sp} = [Ag^+][Cl^-] = (5.0\times10^{-6} + x)(x) = 1.8\times10^{-10}$

$\Rightarrow$ $[Cl^-] = 1.1\times10^{-5}$ M (slightly decreased)

$[Ag^+] = 1.6\times10^{-5}$ M (slightly increased)

$Cl^-(aq)$/Cl(total) = $Cl^-(aq)/(Cl^-(aq)$+AgCl(*s*))

= $(1.1\times10^{-5}$ M)(0.200 L)/1.00×10^{-4} mol = 0.022 = 2.2%

Similarly,

$[Ag^+] = 5.0\times10^{-6} + x$, $[Br^-] = x$

$K_{sp} = [Ag^+][Br^-] = (5.0\times10^{-6} + x)(x) = 3.3\times10^{-13}$

$x < 5.0\times10^{-6}$; therefore, $(5.0\times10^{-6})(x) = 3.3\times10^{-13}$

$\Rightarrow$ $[Br^-] = 6.6\times10^{-8}$ M (significant decrease from 5.7×10^{-7} M)

$[Ag^+] = 5.1\times10^{-6}$ M (significant increase from 5.7×10^{-7} M)

$Br^-(aq)$/Br(total) = $Br^-(aq)/(Br^-(aq)$+AgBr(*s*))

= $(6.5\times10^{-8}$ M)(0.200 L)/1.00×10^{-4} mol = 1.3×10^{-4} = 0.013%

7-5. AgBr will precipitate first. Theoretically, AgBr will begin to precipitate when the Ag^+ concentration reaches 3.3×10^{-10} M. At this concentration of Ag^+, AgCl will not precipitate.

AgBr: $[Ag^+] = K_{sp}/[Br^-] = 3.3\times10^{-13}/1.0\times10^{-3} = 3.3\times10^{-10}$ M

This corresponds to 3.3×10^{-8} L of the Ag^+ solution, which is much less than the smallest volume one can deliver with a micropipet.

7-6. This problem can be solved using the mass conservation relations. Or the solution can be simplified as shown below.

A = total amount of Ag = $[Ag^+]_0 V_{add}$ = $(1.00\times10^{-3}$ M$)V_{add}$

B = total amount of Br = $[Br^-]_0 V_{orignal}$ = $(1.00\times10^{-3}$ M)(0.100L) = 1.00×10^{-4} mol

C = total amount of Cl = $[Cl^-]_0 V_{orignal}$ = $(1.00\times10^{-3}$ M)(0.100L) = 1.00×10^{-4} mol

$A = [Ag^+]\, V_{tot} + n_{AgCl(s)} + n_{AgBr(s)}$ (1)

$B = [Br^-]\, V_{tot} + n_{AgBr(s)}$ (2)

$C = [Cl^-]\, V_{tot} + n_{AgCl(s)}$ (3)

$K_{sp}(AgBr) = [Ag^+][Br^-]$ (4)

$K_{sp}(AgCl) = [Ag^+][Cl^-]$ (5)

▶ V_{add} = 100 mL, V_{tot} = 200 mL (total Ag = 1.00×10^{-4} mol)

Assume that all Ag^+ are used to precipitate Br^- as AgBr(*s*).

$[Ag^+] = [Br^-] = 0$, $[Cl^-] = 5.0\times10^{-4}$ M, AgBr = 1.00×10^{-4} mol, AgCl = 0

At equilibrium,

$[Ag^+] = K_{sp}(AgCl)/[Cl^-] = 3.6\times10^{-7}$ M

$[Br^-] = K_{sp}(AgBr)/[Ag^+] = 9.2\times10^{-7}$ M

total Ag = $Ag^+(aq)$ + AgBr + AgCl, total Br = $Br^-(aq)$ + AgBr

Since total Ag = total Br, $Ag^+(aq)$ + AgCl = $Br^-(aq)$

AgCl = $([Br^-] - [Ag^+])V_{tot}$ = $[(9.2 - 3.6)\times10^{-7}$ M](0.200 L)

= 1.1×10^{-7} mol (0.11% of the total Cl)

$[Cl^-] = 5.0\times10^{-4}$ M (still valid, because very little AgCl is formed)

AgBr = 1.00×10^{-4} mol (still valid, because $[Br^-]$ is small)

▶ V_{add} = 200 mL, V_{tot} = 300 mL (total Ag = 2.00×10^{-4} mol)

Assume complete precipitation of Br^- and Cl^- with Ag^+

$[Ag^+] = [Br^-] = [Cl^-] = 0$, AgBr = 1.0×10^{-4} mol, AgCl = 1.0×10^{-4} mol

At equilibrium,

$[Ag^+] = [Br^-] + [Cl^-] = K_{sp}(AgCl)/[Ag^+] + K_{sp}(AgBr)/[Ag^+]$

$[Ag^+] = 1.3\times10^{-5}$ M

$[Br^-] = K_{sp}(AgBr) / [Ag^+] = 2.5\times10^{-8}$ M

$[Cl^-] = K_{sp}(AgCl) / [Ag^+] = 1.3\times10^{-5}$ M

AgBr = 1.00×10^{-4} mol - $[Br^-]V_{tot}$ = 1.00×10^{-4} mol

AgCl = 1.00×10^{-4} mol - $[Cl^-]V_{tot}$ = 9.6×10^{-5} mol

▶ V_{add} = 300mL, V_{tot} = 400mL (total Ag = 3.00×10^{-4} mol)

Assume complete precipitation of Br^- and Cl^- with Ag^+.

$[Ag^+] = 2.5\times10^{-4}$ M, $[Br^-] = [Cl^-] = 0$, AgBr = 1.0×10^{-4} mol, AgCl = 1.0×10^{-4} mol

$[Br^-] = K_{sp}(AgBr)/[Ag^+] = 1.3\times10^{-9}$ M

$[Cl^-] = K_{sp}(AgCl)/[Ag^+] = 7.2\times10^{-7}$ M

AgBr = 1.00×10^{-4} mol - $[Br^-]V_{tot}$ = 1.00×10^{-4} mol

AgCl = 1.00×10^{-4} mol - $[Cl^-]V_{tot}$ = 9.97×10^{-5} mol

V_{add}	% Br in solution	% Br in precipitate	% Cl in solution	% Cl in precipitate	% Ag in solution	% Ag in precipitate
100 mL	0.18	99.8	99.9	0.11	0.07	99.9
200 mL	0.007	100	4.0	96	2.0	98.0
300 mL	0.0005	100	0.3	99.7	33.3	66.7

Problem 8: Physical methods for determination of Avogadro's number

8-1. (a) volume of particle = $(4 \times 3.14/3)(0.5 \times 10^{-6}/2)^3$ m^3 = 6.54×10^{-14} cm^3

effective mass = $(6.54 \times 10^{-14}$ cm$^3)(1.10 - 1.00)$ g/cm^3 = 6.54×10^{-15} g

(b) $mg(h - h_o)/k_BT = 1$

k_B = $(6.54 \times 10^{-18}$ kg$)(9.81$ m s$^{-2})(6.40\times10^{-5}$ m$)/293.15$ K

= 1.40×10^{-23} J K^{-1}

(c) Avogadro's number = R/k_B

= $(8.314$ J mol^{-1} K$^{-1})/(1.40 \times 10^{-23}$ J K$^{-1})$ = 5.94×10^{23} mol^{-1}

8-2. Length of the edge of a unit cell = $2 \times 2.819 \times 10^{-8}$ cm = 5.638×10^{-8} cm

volume of a unit cell = $(5.638 \times 10^{-8}$ cm$)^3$ = 1.792×10^{-22} cm^3

volume per Na^+ plus Cl^- = 1.792×10^{-22} cm^3 /4 = 4.480×10^{-23} cm^3

formula weight of NaCl = 22.99 + 35.45 = 58.44

molar volume of the crystal = 58.44 g/2.165 g cm^{-3} = 26.99 cm^3

Avogadro's number = $(26.99$ cm$^3)/(4.480 \times 10^{-23}$ cm$^3)$ = 6.025×10^{23}

8-3. Avogadro's number = 96496 C/1.593×10^{-19} C = 6.058×10^{23}

Problem 9: An electrochemical method for determination of Avogadro's number

9-1. anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2\ e^-$; cathode : $2\ H^+\ (aq) + 2\ e^- \rightarrow H_2(g)$

9-2. total charge = (0.601 A)(1 C s^{-1}/1 A)(1802 s) = 1083 C

9-3. number of electrons = (1083 C)(1 electron/1.602×10^{-19} C) = 6.760×10^{21}

9-4. number of copper atoms = (6.760×10^{21})/2 = 3.380×10^{21}
mass of a copper atom = 0.3554 g/3.380×10^{21} = 1.051×10^{-22} g

9-5. Avogadro's number = 63.546 g/1.051×10^{-22} g = 6.046×10^{23}

9-6. Percent error: (6.046×10^{23} - 6.022×10^{23})/(6.022×10^{23}) = 0.4 %

9-7. Weight of H_2 evolved = (1 g)(6.760×10^{21}/6.02×10^{23}) = 0.011 g
Collecting and weighing such a small amount of any gas is not practical considering buoyancy correction.

Problem 10: Enthalpy, entropy, and stability

10-1. (a) K_{eq} and ΔG (b) ΔH (c) ΔS (d) K_{eq} (e) ΔG (f) ΔH

10-2. From $\Delta G = -RT \ln K_p$, ΔG is 1.52 kcal/mol for $Me_3P{\cdot}BMe_3$ and 0.56 kcal/mol for $Me_3N{\cdot}BMe_3$. $Me_3P{\cdot}BMe_3$ is more stable (less likely to dissociate) than $Me_3N{\cdot}BMe_3$ at 100℃.

10-3. $\Delta G = \Delta H - T\Delta S$
$\Delta H_{373} = \Delta G_{373} + 373\ \Delta S_{373} \approx \Delta G_{373} + 373\ \Delta S°$,
$Me_3N{\cdot}BMe_3$: ΔH = 0.56 kcal/mol + (373 K)(45.7 cal/mol·K) = 17.6 kcal/mol
$Me_3N{\cdot}PMe_3$: ΔH = 1.52 kcal/mol + (373 K)(40.0 cal/mol(K) = 16.4 kcal/mol

More heat is needed to dissociate $Me_3N{\cdot}BMe_3$. Therefore, the N-B central bond is stronger.

10-4. $Me_3N{\cdot}BMe_3$:

ΔH = 17.6 kcal/mol $- T\Delta S = -$ (373)(45.7) = -17.05 kcal/mol

ΔG = 0.56 kcal/mol

$Me_3P{\cdot}BMe_3$:

ΔH = 16.4 kcal/mol $- T\Delta S = -$ (373)(40.0) = -14.92 kcal/mol

ΔG = 1.52 kcal/mol

Enthalpy change is larger for $Me_3N{\cdot}BMe_3$; however, larger increase in the entropy term leads to a smaller increase in Gibbs free energy for $Me_3N{\cdot}BMe_3$.

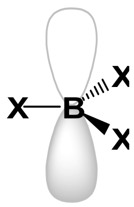
10-5. 17600 cal/mol – (45.7 cal/mol·K) T > 16400 cal/mol – (40.0 cal/mol·K) T

5.7 (cal/mol·K) T < 1200 cal/mol

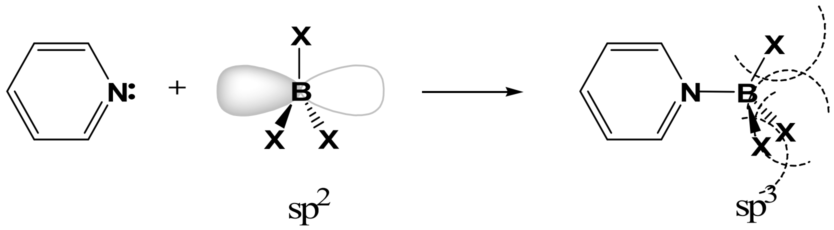
T < 210K (-63℃)

Problem 11: Lewis acids and bases

11-1. Central B has sp^2 hybridization and BX_3 is triangular.



11-2. When an adduct is formed with pyridine, the structure around the central boron becomes tetragonal sp^3 hybrid type (tetrahedron) structure. This structural change will induce steric hindrance around boron which is more pronounced with larger groups (i.e., iodines) and adduct formation is not preferred. Therefore, BF_3 is predicted to show the greatest preference to form adduct. (BF_3 is expected to show the strongest Lewis acidity)



11-3. The more electronegative halogen is expected to effectively remove electron density from the central boron and increase acidity.
Lewis acidity: $BF_3 > BCl_3 > BBr_3$

11-4. Like neutralization that occurs between HCl and NaOH, the reaction producing stable acid-base adduct is expected to be exothermic. The enthalpy change will be the largest for the strongest Lewis acid, BF_3.

11-5.

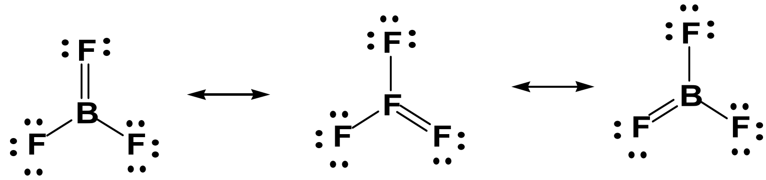
	BF_3	BCl_3	BBr_3	
$\Delta H_3 = \Delta H_1 + \Delta H_2$;	- 31.7	- 39.5	- 44.5	(kcal/mol)

The actual order of acidity is opposite from prediction based on the electronegativity of the halides.

11-6. A = $BF_3 \cdot H_2O$
B = $B(OH)_3$, C = 3 HX (3 HCl or 3 HBr)

Strong Lewis acids such as BCl_3 and BBr_3 can activate O-H bonds in H_2O molecule to produce $B(OH)_3$ by releasing HX. Dative π-bonding with lone pair electrons of O, which have a similar energy level, can stabilize $B(OH)_3$ as explained in 11-7.

11-7. Empty p_z-orbital in boron can accept a dative π-bond from the lone pair electrons of fluorine, which satisfies the 'octet rule' for boron and shortens the boron-fluorine bond distance.



Since resonance structures of this kind are not possible in the adduct compounds, effective resonance will reduce the tendency for pyridine adduct formation.

The ability to form dative π-bonding appears to decrease sharply in the heavier elements due to the energy differences between B and X. Resonance of this dative π-bonding should be of lesser importance in the chloride and least importance in the bromide. These resonance structures having dative π-bonding are sufficiently large so as to reverse the trend expected from the relative inductive effects and the steric effects from the adduct formations.

Problem 12: Solubility equilibrium in a buffer solution

12-1. 440 mL H_2S in 100 mL of water = 4.4 L H_2S in 1 L of water = 0.20 M

12-2. For approximation, the concentration of all anions in (5) except $[Cl^-]$, which is 0.02, can be crossed out. Thus (5) becomes

$$[H^+] + 2[Fe^{2+}] = [Cl^-] = 0.020 \qquad (6)$$

Combine (2) and (3): $[H^+]^2 [S^{2-}]/[H_2S] = 1.24 \times 10^{-21}$

Since $[H_2S] = 0.2$, one gets $[H^+]^2 [S^{2-}] = 2.48 \times 10^{-22}$ (7)

Combine (1) and (7): $[H^+]^2 (8.0 \times 10^{-19}/[Fe^{2+}]) = 2.48 \times 10^{-22}$

$[H^+]^2 = 3.1 \times 10^{-4}\ [Fe^{2+}]$ (8)

Combine (6) and (8) and solve for $[H^+]$:

$[H^+] = 0.0176$ pH = 1.75

$[Fe^{2+}] = (0.020 – 0.0176)/2 = 0.0012$ (12% remains in solution)

Check: $[HS^-] = (9.5 \times 10^{-8})[H_2S]/[H^+] = 1.1 \times 10^{-6} << [Cl^-] = 0.02$

$[S^{2-}] = (1.3 \times 10^{-14})[HS^-]/[H^+] = 2.5 \times 10^{-18}$

$[OH^-] = 5.7 \times 10^{-13}$

Eq. (8) shows that 10-fold decrease in $[H^+]$ increases $[Fe^{2+}]$ 180-fold.

12-3. From $[H^+]^2 = 3.1 \times 10^{-4}\ [Fe^{2+}]$,

$[H^+] = [(3.1 \times 10^{-4})(1 \times 10^{-8})]^{1/2} = 1.76 \times 10^{-6}$ pH = 5.75

12-4. original HOAc = 0.10 M x 100 mL = 10 mmol

Henderson-Hasselbalch eq for the HOAc-OAc^- buffer at pH 5.75

$pH = 5.75 = pK + \log [OAc^-]/[HOAc] = 4.74 + \log [OAc^-]/[HOAc]$

initial Fe^{2+} = 0.01 M x 100 mL = 1 mmol

H^+ produced upon precipitation of 1 mmol Fe^{2+} = 2 mmol

OAc^- consumed by H^+ produced = 2 mmol

$\log [OAc^-]/[HOAc] = 5.75 - 4.74 = 1.01$

Let x = original mmol OAc^-

$(x - 2)/(10 + 2) = 10^{1.01} = 10.2$, x = 124 mmol

$[OAc^-]$ = 124 mmol/100 mL = 1.24 M

12-5. pH = 4.74 + log (1.24/0.10) = 5.83

Problem 13: Redox potential, Gibbs free energy, and solubility

13-1. $Ag^+(aq) + e^- \rightarrow Ag(s)$ $E° = 0.7996$ V

$\Delta G° = \Delta G_f°(Ag(s)) + \Delta G_f°(e^-) – \Delta G_f°(Ag^+(aq)) = – \Delta G_f°(Ag^+(aq)) = – F\Delta E°$

Therefore, $\Delta G_f°(Ag^+(aq)) = F\Delta E°$ = 77.15 kJ/mol

13-2. $Ag^+(aq) + 2\ NH_3(aq) \rightarrow Ag(NH_3)_2^+(aq)$

$\Delta G° = \Delta G_f°(Ag(NH_3)_2^+(aq)) – \Delta G_f°(Ag^+(aq)) – 2\ \Delta G_f°(NH_3(aq))$

$= –17.12$ kJ – 77.15 kJ – (2)(–26.50) kJ = – 41.27 kJ

$\ln K_f = \dfrac{-\Delta G^\circ}{RT} = 16.65$ $\quad K_f = \dfrac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = e^{16.65} = 1.7 \times 10^7$

13-3. $AgBr(s) \rightarrow Ag^+(aq) + Br^-(aq)$ $\quad \Delta E° = (0.0713 – 0.7996)\ V = –0.7283$ V

$\ln K_{sp} = \dfrac{-\Delta G^\circ}{RT} = \dfrac{nF\Delta E^\circ}{RT} = –28.17$

$K_{sp} = [Ag^+][Br^-] = e^{–28.347} = 4.8_9 \times 10^{–13}$

13-4. Let us assume $[Ag^+] << [Ag(NH_3)_2^+]$.

$AgBr(s) \rightarrow Ag^+(aq) + Br^-(aq)$ $\quad K_{sp} = 4.8_9 \times 10^{-13}$

$Ag^+(aq) + 2\ NH_3(aq) \rightarrow Ag(NH_3)_2^+(aq)$ $\quad K_f = 1.7 \times 10^7$

$AgBr(s) + 2\ NH_3(aq) \rightarrow Ag(NH_3)_2^+(aq) + Br^-(aq)$ $\quad K = K_{sp} K_f = 8.3_1 \times 10^{-6}$

Initial	0.100	0	0
Change	–2*S*	+*S*	+*S*
Equilibrium	0.100 – 2*S*	*S*	*S*

$$K = \frac{S^2}{(0.1-2S)^2} = 8.3_1 \times 10^{-6} \quad \rightarrow \quad \frac{S}{(0.1-2S)} = 2.88 \times 10^{-3}$$

$S = [Ag(NH_3)_2^+] = [Br^-] = 2.9 \times 10^{-4}$ M

$[Ag^+] = K_{sp}/[Br^-] = 1.7 \times 10^{-10}$ M $<< [Ag(NH_3)_2^+]$

Thus, the solubility of AgBr is 2.9×10^{-4} M

13-5. $[Br^-] = K_{SP} / [Ag^+] = 4.89 \times 10^{-13} / 0.0600 = 8.15 \times 10^{-12}$

$$\Delta E° = \Delta E + \frac{RT}{nF} \ln \frac{[Br^-]^2[H_3O^+]^2}{P_{H_2}}$$

$$= 1.721 + \frac{0.0592}{2} \log_{10} \frac{(8.15 \times 10^{-12})^2 1^2}{1} = 1.065 \text{ V}$$

13-6. In order to estimate the solubility of $Br_2(aq)$, we need to calculate the Gibbs free energy of the reaction:

$Br_2(l) \rightarrow Br_2(aq)$ $\quad \Delta G°?$

From (e), $Br_2(l) + 2\ e^- \rightarrow 2\ Br^-(aq)$

$E_1° = 1.065$ V, $\Delta G_1° = -2FE_1° = -2.130F$ V

Let us first calculate $E_2°$ for the half-cell reaction:

$Br_2(aq) + 2\ e^- \rightarrow 2\ Br^-(aq)$ $\quad E_2°, \Delta G_2° = -2FE_2°$

From the Latimer diagram,

$BrO_3^-(aq) + 6\ H_3O^+(aq) + 6\ e^- \rightarrow Br^-(aq) + 9\ H_2O(l)$ $\quad E_3° = 1.441$ V

$BrO_3^-(aq) + 5\ H_3O^+(aq) + 4\ e^- \rightarrow HOBr + 7\ H_2O(l)$ $\quad E_4° = 1.491$ V

$2\ HOBr + 2\ H_3O^+(aq) + 2\ e^- \rightarrow Br_2(aq) + 4\ H_2O(l)$ $\qquad E_5° = 1.584$ V

Then, $2\ BrO_3^-(aq) + 12\ H_3O^+(aq) + 10\ e^- \rightarrow Br_2(aq) + 18\ H_2O(l)$

$$E_6° = (2\ x 4E_4° + 2E_5°)/10 = 1.5096 \text{ V}$$

Similarly, $Br_2(aq) + 2\ e^- \rightarrow 2\ Br^-(aq)$

$$E_2° = (2\ x\ 6E_3° - 10E_6°)/2 = 1.098 \text{ V}$$

(Note that $6 \text{ x } E_3° = 4 \text{ x } E_4° + 1 \text{ x } E_5° + 1 \text{ x } E_2°$)

Then, $\Delta G_2° = -2\Delta E_2° = -2.196F$ V

Finally, $\Delta G° = \Delta G_1° - \Delta G_2° = 0.066F$ V = 6368 J/mol

Therefore,

$$[Br_2(aq)] = K = e^{\frac{-\Delta G°}{RT}} = e^{-2.569} = 0.077 \text{ (M)}$$

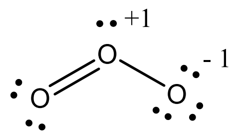
Problem 14: Measuring the ozone level in air

14-1. $3I^- \rightarrow I_3^- + 2e^-$

$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$

$3I^- + O_3 + 2H^+ \rightarrow I_3^- + O_2 + H_2O$

14-2.



14-3. The absorbance is given by

$A = -\log T = -\log(I_{sample}/ I_{blank}) = \log (R_{sample}/R_{blank})$

$= \log (19.4 \text{ k}/12.1 \text{ k}) = 0.205$

$[I_3^-] = A / \varepsilon b = 0.205/(240{,}000\ M^{-1}cm^{-1})(1.1\ cm) = 7.76\times10^{-7}$ M

Number of moles $O_3 = V_{sample}\ [I_3^-] = (0.01\ L)(7.76\times10^{-7}\ mol/L) = 7.76\times10^{-9}$ mol

14-4. The number of moles of air sampled

$= PV/RT = P(t_{sampling}\ F)/RT$

$= (750\ torr)(30\ min)(0.250\ L/min)/(62.4\ torr{\cdot}L\ mol^{-1}K^{-1})(298\ K) = 0.302$ mol

The concentration of O_3 in ppb = $(7.76 \times10^{-9}\ mol / 0.302\ mol) \times 10^9 = 25.7$

Problem 15: Lifesaving chemistry of the airbag

15-1. $:\overset{-}{\underset{..}{N}}=\overset{+}{N}=\overset{-}{\underset{..}{N}}:\quad :N\equiv N:$

15-2. moles of $N_2 = PV/RT$

$= (1.25\text{ atm})(15\text{L})/(0.08206\text{ L atm K}^{-1}\text{mol}^{-1})(323\text{K}) = 0.707$

2 moles of sodium azide generate 3.2 moles of nitrogen.

Weight of sodium azide needed to generate 0.707 moles of nitrogen

$= (2)(0.707/3.2)(65\text{g}) = 29\text{ g}$

15-3. $4\ C_3H_5(NO_3)_3 \rightarrow 6\ N_2 + O_2 + 12\ CO_2 + 10\ H_2O$

$Pb(N_3)_2 \rightarrow Pb + 3\ N_2$

In all three reactions, the reactants are solid or liquid with small volume. A large volume of nitrogen gas is produced. Nitroglycerin produces other gases. The nitrogen molecule has a triple bond and is very stable. Thus, the reactions are highly exothermic, so that gases produced expand rapidly.

15-4. $2\ NaN_3 + H_2SO_4 \rightarrow 2\ HN_3 + Na_2SO_4$

15-5. $NaN_3 = 60\text{g} / (65\text{g/mol}) = 0.923\text{ mol}$

$H_2SO_4 = 3\text{ mol/L} \times 0.1\text{ L} = 0.3\text{ mol}$

$HN_3 = (2)(0.3\text{ mol})(43.0\text{ g/mol}) = 26\text{ g}$

Problem 16: Catalysis for the synthesis of ammonia

16-1 $\Delta S^{o} = (2)(192.5) – (191.6 + 3\text{x}130.7) = - 198.7\text{ J/(K}\cdot\text{mol)}$

The reaction must be exothermic and produce enough heat to increase the entropy of the surroundings and thereby offset the decrease in system entropy.

16-2 Combination of hydrogen with a more electronegative element will be more exothermic.

$H_2O(g)$: - 241.82 kJ/mol

$HF(g)$: - 271.1 kJ/mol

$NH_3(g)$: - 46.11 kJ/mol

16-3. $\Delta S_{tot} = \Delta S_{sys} + \Delta S_{sur} = \Delta S_{sys} - \Delta H_{sys}/T$

$= 198.7$ J/K + $(92.22 \times 10^3$ J/298 K) = + 110 J/K

16-4. $NH_3(g)$: - 46.11 kJ/mol

$k_1 = A \exp(-E_a/RT) = 10^{13} \exp[-940 \times 10^3/(8.3145 \times 1073)] = 1.74 \times 10^{-33}$ sec^{-1}

$k_2 = A \exp(-E_a/RT) = 10^{13} \exp[-470 \times 10^3/(8.3145 \times 1073)] = 1.32 \times 10^{-10}$ sec^{-1}

$k_2/k_1 = 7.6 \times 10^{22}$

16-5. mass of cube = 7.86 g/cm^3 x $(10^{-4}$ cm$)^3$ = 7.86 x 10^{-15} kg

number of cubes in 1 kg = 1 kg/(7.86 x 10^{-15} kg) = 1.27 x 10^{14}

surface area of Fe powder = 6 x 10^{-12} m^2 x 1.27 x 10^{14} = 763 m^2

area for N_2 adsorption = 0.16 x 10^{-18} m^2

N = area of Fe powder / area for N_2 = 4.77 x 10^{21} = 7.92 x 10^{-3} mole

16-6. 1 kg/(0.5 kg/mole) = 2 mole = 1.20 x 10^{24}

16-7. 8 x 30.5 kJ/mole = 244 kJ

E(nitrogenase) < E(chemical industry)

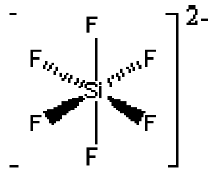
Problem 17: From sand to semiconductors

17-1. Si : 1/8 × 8 + 1/2 × 6 + 1 × 4 = 8

O : 1 × 16 = 16

17-2. sp^3 ; 109.5°

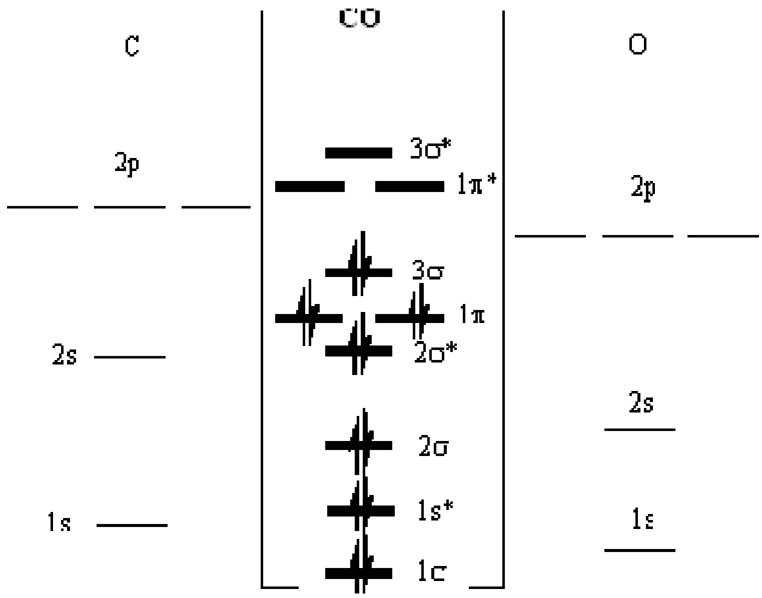
17-3. octahedral:



17-4. Since Lewis structure of the gas shows the formal charges, it should not be O=C=O, but :C≡O: where C has the formal charge of -1 and O has the formal charge of +1. Therefore, the balanced equation for the reaction is

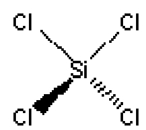
$$SiO_2(s) + 2C(s) \rightarrow Si(s) + 2CO(g)$$

17-5.

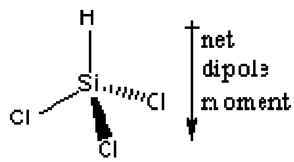


17-6. $Si(s) + 2Cl_2(g) \rightarrow SiCl_4(l)$: from the *Merck Index*
Schenk in *Handbook of Preparative Inorganic Chemistry* Vol. 1, G. Brauer, Ed. (Academic Press, New York, 2nd ed., 1963) pp 682-683.

17-7. Tetrahedral



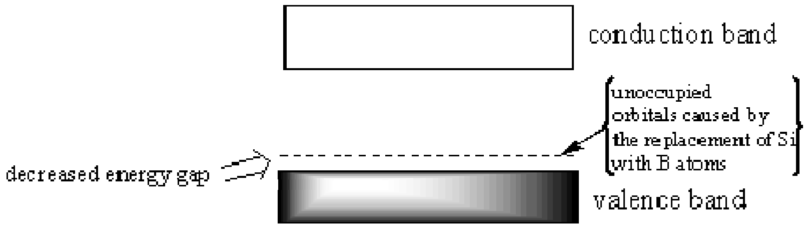
17-8. C = $SiHCl_3$, polar



17-9. (1 g/32.066 g/mol)×0.1×10^{-9}×6.02×10^{23} = 1.9×10^{12}

17-10. In a Si wafer doped with B atoms, holes exist that neighboring electrons can move into, thus causing electrical conductivity. Therefore, holes are the charge carriers. This kind of doped-semiconductor is the p-type semiconductor.

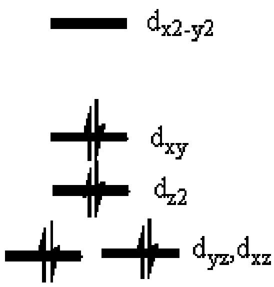
17-11.



Problem 18: Self-assembly

18-1. square planar

18-2. Ni^{2+}, d^8, square planar, diamagnetic



18-3. a long alkyl side chain: $-C_{16}H_{33}$.

18-4. hydrophobicity due to the long alkyl chains

18-5. bond a

18-6. bonds b and d are shortened upon reduction.

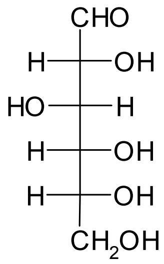
18-7. coordination number of 6

18-8. π-π stacking interactions

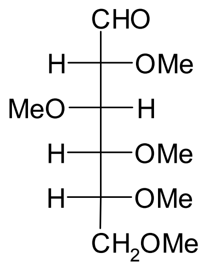
Problem 19: Stereochemistry (Organic synthesis – 1)

19-1.

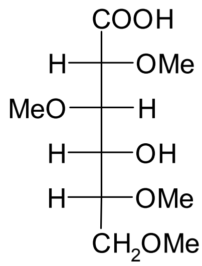
B



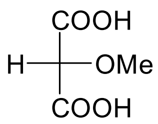
D



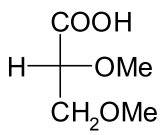
E



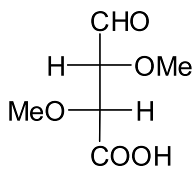
F



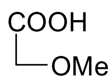
F’



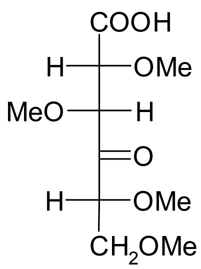
G



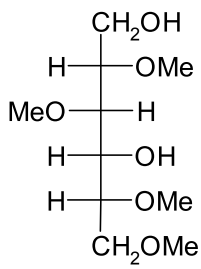
H



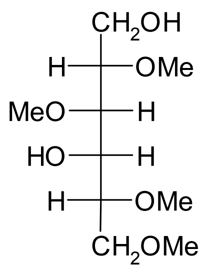
I



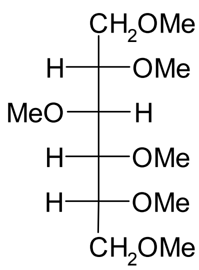
J



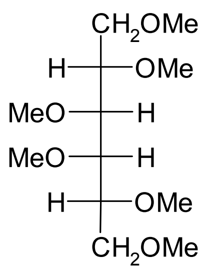
K



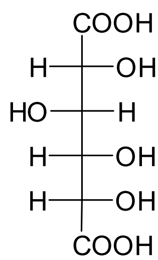
L



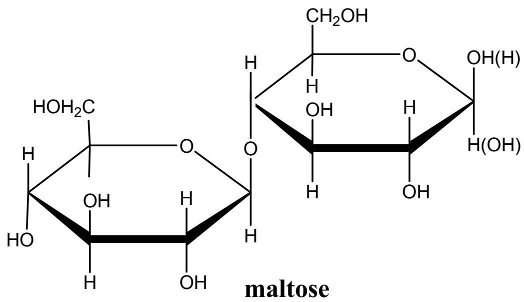
M



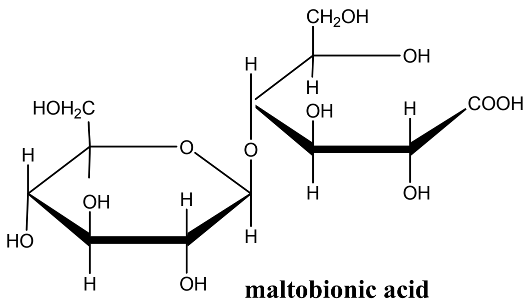
N



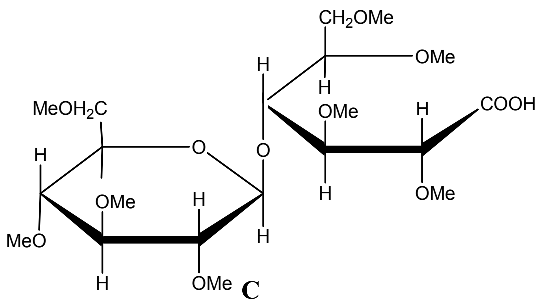
19-2.



maltose

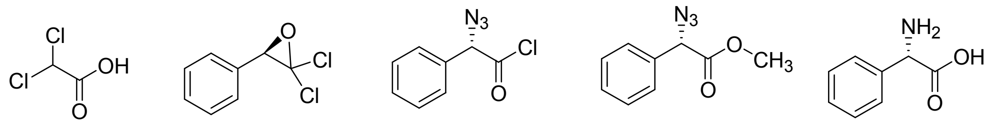


maltobionic acid



C

Problem 20: Total synthesis (Organic synthesis – 2)

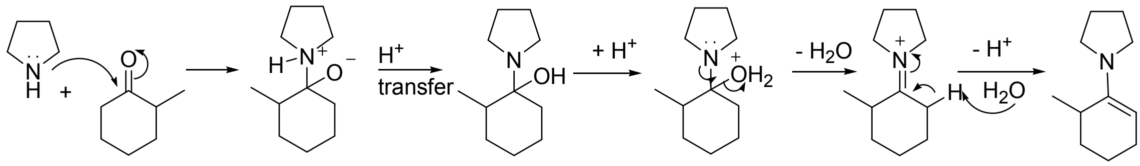


A **B** **C** **D** **E**

configuration : **S**

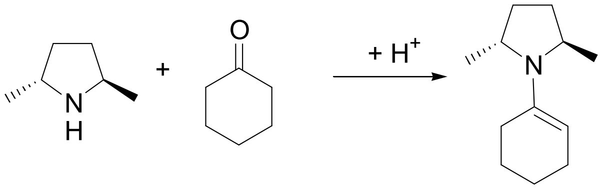
Problem 21: Enamine chemistry (Organic synthesis – 3)

21-1.



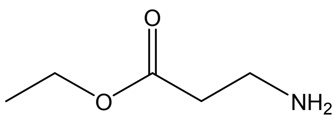
21-2. Normally, acid catalyzes the enamine formation as shown in 21-1. However, if too much acid is present, the basic amine (nucleophile) is completely protonated so the initial nucleophilic addition step cannot occur.

21-3. An enamine prepared from a single enantiomer of the chiral secondary amine is chiral, and thus the Michael addition reaction can proceed from only one side of enamine to yield a single enantiomeric product.

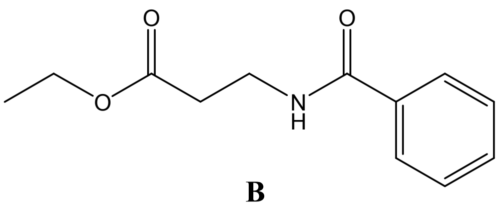


Problem 22: Oxidation and reduction in organic synthesis

22-1.

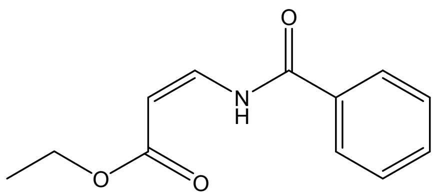


A



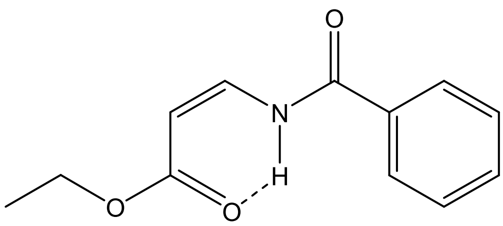
B

22-2.



C

22-3. The cis-conformation of the olefin allows the strong hydrogen bonding between the proton of the amide and the carbonyl oxygen of the ester as shown in the following structure.



The strong hydrogen bonding moved the chemical shift of the amide proton toward further down-field.

Problem 23: Antifreeze proteins

23-1. For freezing point depression, $\Delta T = -K_f m$

The molal concentration m is obtained by

– 20 = – 1.86 m,

m = 10.75 mol/kg

The weight of the glycerol in 1 kg of water is

w = *m* x *MW* = 10.75 x 92 = 989 kg.

Therefore, glycerol would be about 50 % by weight.

This is a ridiculously large number indicating that something else is also required to avoid freezing.

Osmotic pressure is obtained from the van't Hoff equation, $\pi = cRT$.

Assuming that the molar concentration c is approximately the same as the molal concentration obtained above,

Osmotic pressure = 10.75 x 0.082 x (273 – 20) = 223 atm

The osmotic pressure is extremely high, and the organism may not be stable.

23-2. From Figure 1, the glycerol content in January is

2500 μmol/g = 2.5 mol/kg = (230 g glycerol)/ (1 kg water).

Therefore, the glycerol fraction is 18.7 % of total weight.

Freezing point depression at this concentration is

– 2.5 x 1.86 = – 4.7^{o}C,

which is significantly higher than the temperature in January.

23-3. Threonine and aspartate side chains can contact each other through their oxygen and hydrogen groups to form stable hydrogen bonds. The hydrogen bonds of these side chains might preferably interact with water molecules of the ice particle surfaces, thus inhibiting ice crystal growth.

Problem 24: The human body

24-1. average atomic weight of three atoms in a water molecule = 18/3 = 6

average atomic weight of atoms in other molecules is about the same.

For example, consider carbohydrate, $C(H_2O)$. 28/4 = 7

So, let's assume that the human body is composed of only water.

60 kg of water = 10,000 moles of atoms = 6×10^{27} atoms or about 10^{28} atoms

24-2. Assume that the density of the human body is 1 g/cm^3.

volume of body = 6×10^{-2} m^3

volume of a cell = 6×10^{-16} m^3

length of a cell = 8×10^{-6} m (about 10 micrometers)

24-3. number of atoms in a cell = $10^{28}/ 10^{14} = 10^{14}$

volume per atom in a cell = 6×10^{-16} m^3 / 10^{14} = 6×10^{-30} m^3

distance between two atomic nuclei = 2×10^{-10} m = 2 Angstroms

24-4. volume of a mole of water = 18×10^{-6} m^3

average volume occupied by a water molecule = 3×10^{-29} m^3

distance between center of mass of two water molecules

= 3×10^{-10} m = 3 Angstroms

24-5. volume of a mole of water = 18×10^{-6} m^3

number of atoms in a mole of water = 18×10^{23}

average volume occupied by an atom in water = 10^{-29} m^3

average distance between atomic nuclei in water

= 2×10^{-10} m = 2 Angstroms

Problem 25: Hemoglobin

25-1. 150 g hemoglobin in 1 L

$150\ g/67{,}000\ g\ mol^{-1} = 0.0022\ mol$ $\quad$ $0.0022\ M$

25-2. volume of a mole of air = $22.4 \times 10^{-3}\ m^3$

number of oxygen molecules in above volume

$= (6.02 \times 10^{23})(0.21) = 1.26 \times 10^{23}$

volume of air per oxygen molecule

$= (22.4 \times 10^{-3}\ m^3)/(1.26 \times 10^{23}) = 1.78 \times 10^{-25}\ m^3$

average distance between oxygen molecules = $5.6 \times 10^{-9}\ m$

25-3. solubility = $(1.3 \times 10^{-3}\ mol\ L^{-1}\ atm^{-1})(0.21\ atm) = 2.7 \times 10^{-4}\ mol\ L^{-1}$

number of oxygen molecules in a liter of water

$= (6 \times 10^{23}\ mol^{-1})(\ 2.7 \times 10^{-4}\ mol\ ) = 1.6 \times 10^{20}$

volume of water per oxygen molecule

$= (1 \times 10^{-3}\ m^3)/(1.6 \times 10^{20}) = 6.3 \times 10^{-24}\ m^3$

average distance between oxygen molecules = $1.8 \times 10^{-8}\ m$

25-4. number of oxygen molecules in 1 L of blood

$= (4)(0.0022)(6 \times 10^{23}) = 5.3 \times 10^{21}$

volume of blood per oxygen molecule

$= 10^{-3}\ m^3/\ 5.3 \times 10^{21} = 1.9 \times 10^{-25}\ m^3$

distance between oxygen molecules

$= 5.7 \times 10^{-9}\ m$

25-5. The average molecular weight of amino acids is about 130.

Water is removed upon peptide bond formation.

67,000/(130 – 18) = 600 amino acid residues

Actually hemoglobin has two alpha and two beta chains, each of which consists of 141 residues.

25-6. All life-forms on earth use 20 common amino acids.

25-7. Trypsin hydrolyzes after 2 amino acid residues (arginine and lysine) out of 20 different kinds of amino acids. So, on average the enzyme breaks every 10th peptide bond.

The number of amino acid residues in an average tryptic peptide = 20/2 = 10

25-8. Consider removal of water in the peptide bond formation.

(130 – 18) x 10 + 18 = 1,140 = about 1,000

Problem 26: Mass spectrometry of hemoglobin

26-1. osmotic pressure (freezing point depression is too small, mass spectrometry is not available)

26-2. For a singly charged protein ion (67,435 Da)

electrical energy = eV = $(1.60218 \times 10^{-19}$ C$)(2.0000 \times 10^{4}$ V$) = 3.20436 \times 10^{-15}$ J

26-3. $mv^2/2$ = electrical energy

m = (2)(electrical energy)/v^2

= $(2)(3.20436 \times 10^{-15}$ J$)/(1.0000$ m$/1.3219 \times 10^{-4}$ s$)^2 = 1.11987 \times 10^{-22}$ kg

MW of $[M+H]^+$ = $(1.11987 \times 10^{-22}$ kg$)(6.0221 \times 10^{23}) = 67.440$ kg

MW of hemoglobin = 67,440 – 1 = 67,439

mass accuracy = 67,439/67,434 = 1.000074 74 ppm

26-4. volume of collision cylinder = $\pi d^2 v$

number of molecules in unit volume: $N/V = PN_0/RT$

collision/sec = (volume of collision cylinder)(molecules/unit volume)

= $(\pi d^2 v)(PN_0/RT)$

time between collisions = $1/[(\pi d^2 v)(PN_0/RT)]$

mean free path = speed/time between collisions

= $v/[(\pi d^2 v)(PN_0/RT)]$ = 1 m

$P = (RT/N_0)/[(\pi d^2)(1\text{ m})]$

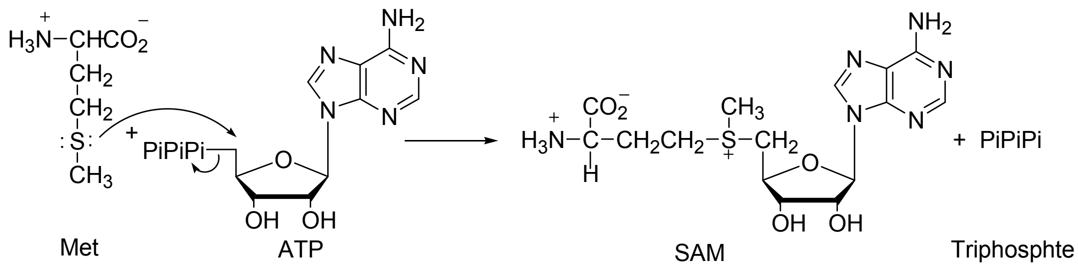
= $(8.314$ J mol^{-1} K$^{-1})(298$ K$)/[(6.02 \times 10^{23}$ mol$^{-1})(3.14)(2 \times 10^{-10}$ m$)^2(1$ m$)]$

= 3.3×10^{-2} Pa = 3.2×10^{-7} atm

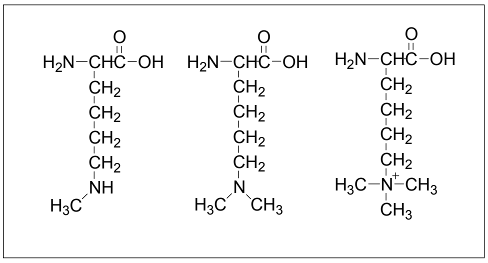
Problem 27: Post-translational modification

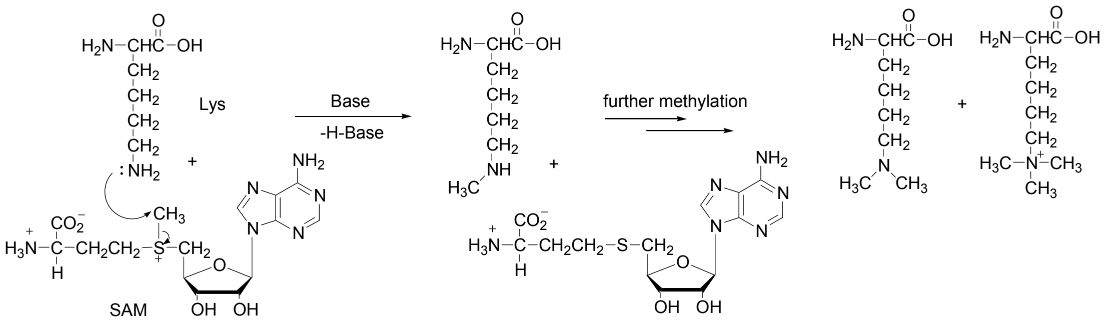
27-1. Lys (K) and Arg (R) provide plausible methylation sites at their side chains, because they can accept more than one methyl groups. Other amino acids side chains with oxygen nucleophile can hold only one methylation.

27-2. Triphosphate group is a good leaving group and sulfur is a good nucleophile. Sulfur of methionine undergoes S_N2 type reaction with ATP with triphosphate as the leaving group to form SAM.



27-3.





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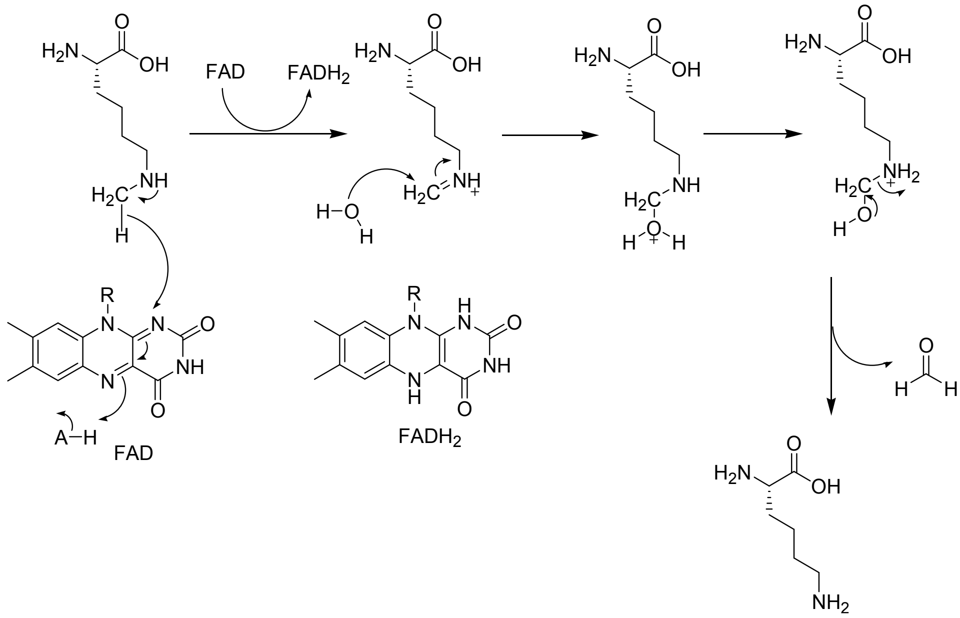


Problem 28: Transition state in enzymatic reactions

28-1. The reduced energy of the transition state can be calculated by comparing ΔG^o (ΔG^o = $-RT$ lnK_{eq}) values between K_D of selected antibody and normal antibody).

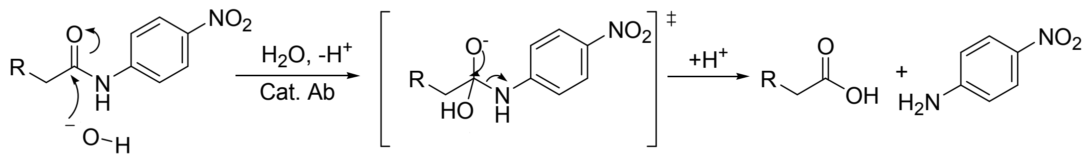
ΔG^o = ($-RT$ ln$K_{D,\ selected}$) - ($-RT$ ln$K_{D,\ normal}$) = $-RT$(ln$K_{D,\ selected}$ - ln$K_{D,\ normal}$)

= -8.32 x 310 x ln ($10^{-13}/10^{-6}$) = 41.6 kJ/mol

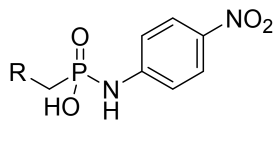
28-2. k_{cat}/k_{uncat} = exp(E_{uncat} - E_{cat}/RT) by Arrhenius equation ($k = A$ exp($-E_a/RT$))

k_{cat}/k_{uncat} = exp(41,600/8.32x310) = 1 x 10^7 (ratio of K_D above)

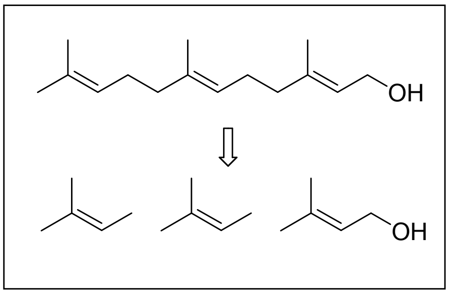
28-3.

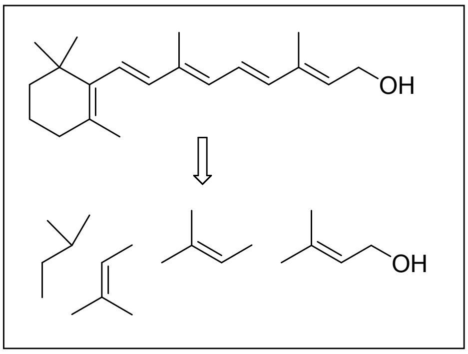


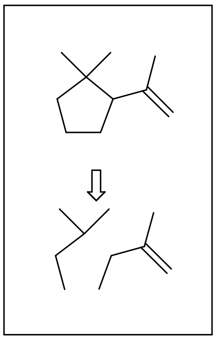
28-4.

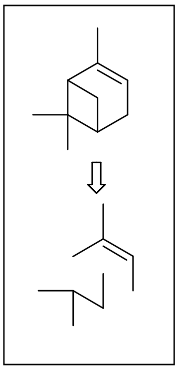


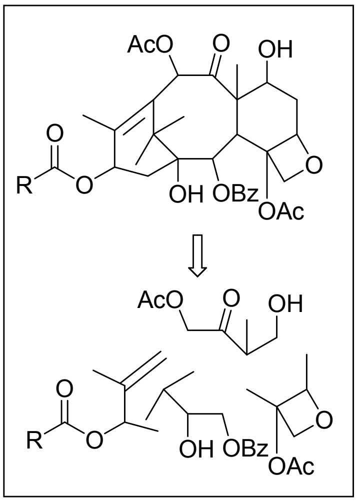
Problem 29: Nature's building blocks

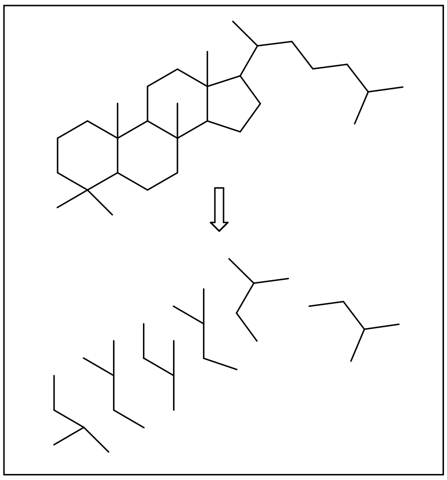




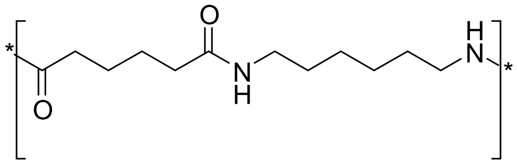




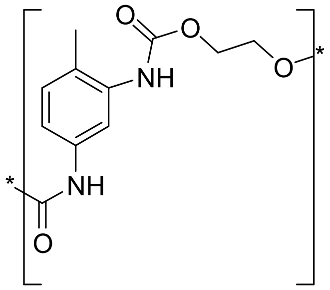




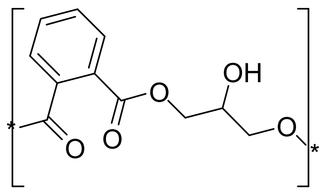
Nylon-6,6

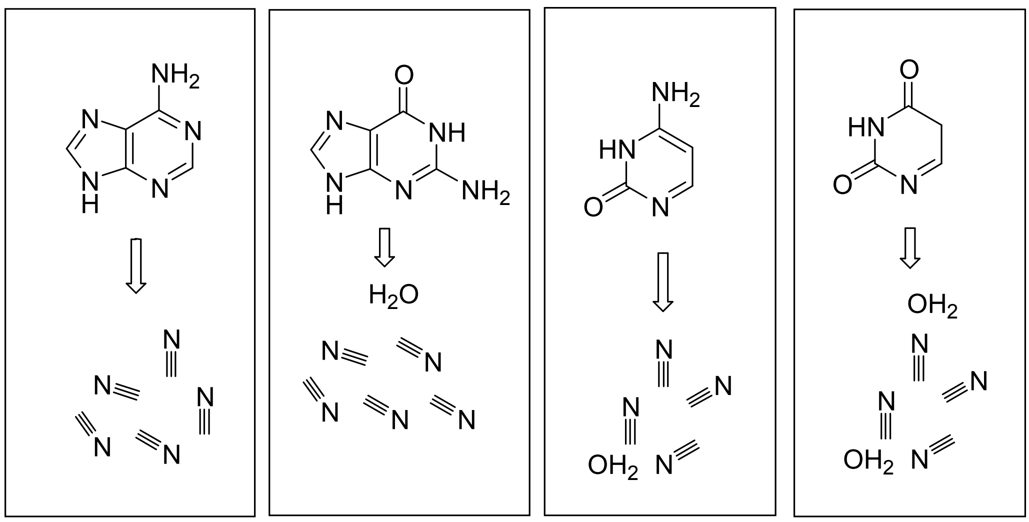


Polyurethane



Glyptal





Problem 30: True or false

True: 2, 3, 7, 8, 9, 11

False: 1, 4, 5, 6, 10, 12