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Constants: $c = 3 \times 10^8$ m/s, $h = 6.63 \times 10^{-34}$ Js, Avogadro No: 6.023×10^{23}, F = 96500 coul
$R = 8.314\ J\ K^{-1}\ mol^{-1} = 0.08205\ L\ atm\ K^{-1}\ mol^{-1}$

Use the following data whenever necessary:

Element:	H	He	B	C	N	O	F	Mg	Al	P	Fe	S
At. No:	1	2	5	6	7	8	9	10	11	15	26	16
At. Wt:	1	7	11	12	14	16	19	24	27	30	56	32

Prepared by General Chemistry Instructors

Good Luck

Part I - Multiple choice questions: (Shade the circle for right choice in the answer sheet)

1. The Principal quantum number is related to the
   (a) Orbital angular momentum (b) Size and shape of the orbital
   (c) Orientation of the orbital (d) Average size of the orbit
2. The quantum number that defines the shape of the orbital occupied by the electron is
   (a) Principal quantum number (b) Azimuthal quantum number
   (c) Magnetic quantum number (d) Spin quantum number
3. The value of azimuthal quantum number for the electrons present in 5s-orbital is
   (a) 0 (b) 1 (c) 2 (d) 5
4. For a multi-electron atom, the energy associated with electrons is s, p, d and f orbitals of a particular principal quantum number is in the order
   (a) s = p = d = f (b) s > p > d > f (c) p > d > f > s (d) d < f < s < p
5. The mass number and atomic number of phosphorus atom are 31 and 15 respectively. The number of neutrons in the nucleus is
   (a) 15 (b) 16 (c) 31 (d) 46
6. The radius of first orbit in hydrogen atom is 0.529 Å. The radius of second orbit is given by
   (a) ½ × 0.529 Å (b) 2 × 0.529 Å (c) 4 × 0.529 Å (d) 8 × 0.529 Å
7. The maximum number of electrons that can be accommodated in a shell is
   (a) 2n (b) n^2 (c) $2n^2$ (d) 2n + 1
8. An atom of silicon with atomic number 14 has the following number of electrons in the outermost shell
   (a) 1 (b) 2 (c) 4 (d) 8

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9. Which one of the following is the most polar
(a) H — F (b) H — Cl (c) H — Br (d) H — I

10. Bond Order of O_2, F_2, N_2 respectively are
(a) 1, 2, 3 (b) 2, 3, 1 (c) 2, 1, 3 (d) 3, 2, 1

11. The hydrogen bromide molecule is formed by
a) The axial p-p overlapping b) The sideways s-p overlapping
c) The axial s- p overlapping d) The sideways s- p overlapping

12. Which of the following complex ion involves d^2sp^3 hybridization for the central atom?
a) $[CoF_6]^{3-}$ b) $[Co(CN)_6]^{3-}$ c) $[FeI_6]^{3-}$ d) $[Co(H_2O)_6]^{3+}$

13. The greater the electronegativity difference between two atoms bonded together, the greater the bond's percentage of,
a) Metallic character b) Ionic character
c) Covalent character d) electron sharing

14. The Gibb's free energy change for non-spontaneous process is
a) Positive b) Negative
c) Zero d) None of these

15. A gas expands isothermally and reversibly. The work done by the gas is
a) Zero b) Minimum c) Maximum d) Equal to heat change

16. The number of unpaired electrons in chromium atom (Z = 24) is
(a) 12 (b) 24 (c) 8 (d) 6

17. After filling the 4p-orbitals, an electron will enter in
(a) 4d (b) 4f (c) 5s (d) 3d

18. The outermost electronic configuration of manganese (at. no. = 25) is
(a) $3d^5\,4s^2$ (b) $3d^6\,4s^1$ (c) $3d^7\,4s^0$ (d) $3d^5\,4s^2$

19. The compounds which contain both ionic and covalent bonds are
(a) $CHCl_3$ and CCl_4 (b) KCl and $AlCl_3$ (c) KCN and NaOH (d) H_2 and CH_4

20. The molecule among CCl_4, PCl_3, SF_4 and NH_3 that does not contain lone pairs of electrons around the central atom is
(a) CCl_4 (b) PCl_3 (c) SF_4 (d) NH_3

21. Which of the following does not obey the octet rule?
(a) PCl_5 (b) H_2O (c) NH_3 (d) CCl_4

22. In a bond between two atoms X and Y, the shared electron pair does not lie in the centre. The bond is
(a) Pi bond (b) non-polar covalent bond
(c) polar covalent bond (d) co-ordinate bond

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23. For the gaseous system A + 2B ⇌ C, the equilibrium concentration are [A] = 0.006 mol litre^{-1}, [B] = 0.12 mol litre^{-1}, [C] = 0.216 mol litre^{-1}. The equilibrium constant for the reaction is,

a) 250 b) 417 c) 125 d) 4×10^{-3}

24. 4 moles of PCl_5, 2 moles of PCl_3 and 3 moles of Cl_2 are taken in a closed vessel. At equilibrium, if the vessel contains 2 moles of PCl_5, the total number of moles in the container is

a) 8 b) 9 c) 10 d) 11

25. For a spontaneous reaction, total entropy change is always

a) Positive b) Negative c) zero d) Infinite

26. For the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ the production of NO is favoured by

a) Increasing pressure b) Decreasing pressure

c) Decreasing the concentration of N_2 and O_2 d) Removing NO

27. Sodium acetate is added to a solution of acetic acid, then pH of solution,

a) Decreases b) Increases c) Remains unchanged d) None of these

28. More acid is added to solution of pH = 5 in order to reduce the pH =2. The increase in hydrogen ion concentration is,

a) 100 times b) 1000 times c) 3 times d) 5 times

29. Enthalpy of formation of HF and HCl are –161kJ and –92kJ respectively. Which of the following statements is incorrect?

a) The affinity of fluorine for hydrogen is greater than the affinity of chlorine for hydrogen

b) HF is more stable than HCl

c) HCl is more stable than HF

d) HF and HCl are exothermic compounds

30. The solubility product of calcium fluoride is 3.2×10^{-11}. The solubility of calcium fluoride in a saturated solution is,

a) 2.0×10^{-4} mole / litre b) 12.0×10^{-3} mole / litre

c) 0.2×10^{-4} mole / litre d) 2.0×10^{-3} mole / litre

31. Consider the following reaction. $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$,

with reference to the above, which one of the following is the correct statement?

a) Zn is reduced to Zn^{2+} ions b) Zn is oxidized to Zn^{2+} ions

c) Zn^{2+} ions are oxidized to Zn d) Cu^{2+} ions are oxidized to Cu

32. The standard electrode potentials of Zn^{+2}/Zn and Ag^{+}/Ag are -0.763 V and + 0.799 V respectively. The standard potential of the cell is

a) 1.562 V b) 0.036V c) -1.562 d) 0.799 V

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33. Three metals A, B and C are in order of decreasing reduction potential. Indicate the true Statement.

a) Atoms of B can reduce ions of C b) Atoms of B can reduce ions of A

c) Atoms of B can reduce atoms of C d) Atoms of B can reduce atoms of A

34. Electrolysis involves oxidation and reduction respectively at,

a) Anode and cathode b) Cathode and anode c) Both electrodes d) None

35. The order of potential of metals in the electrochemical series is Mg < Al < Zn < Cu<Ag. What will happen if a copper spoon is used to stir solution of silver nitrate?

a) The spoon will get coated with Al b) The alloy of Cu and Al is formed

c) The solution becomes blue d) There is no reaction

36. In a galvanic cell, the electrons flow from,

a) Anode to cathode through the solution b) Cathode to anode through the solution

c) Anode to cathode through the external circuit d) Cathode to anode through the external circuit.

37. 22.5 cm^3 of HCl is required to neutralize 15 cm^3 of 0.15M NaOH. What is the pH of the acid?

a) 7 b) 1 c) 14 d) 10

38. The enthalpy of formation of ammonia is – 46.0kJ mol^{-1}. The enthalpy change for the reaction $2NH_3 \rightarrow N_2 + 3H_2$ is

a) –46.0kJ b) +92.0kJ c) – 23.0kJ d) – 92.0kJ

39. The relation between internal energy change ΔU and enthalpy change ΔH and work W is

a) $\Delta H = \Delta U + W$ b) $\Delta U = \Delta H + W$ c) $\Delta U = W - \Delta H$ d) $\Delta H = \Delta U - W$

40. In a gaseous reaction, the correct relation between K_P and K_C is,

a) $K_C = K_P (RT)^{\Delta n}$ b) $K_P = K_C (RT)^{\Delta n}$ c) $K_C / RT = (KP)^{\Delta n}$ d) $K_P / R_T = (K_C)^{\Delta n}$

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Part II - Answer all questions:

1. Calculate the Empirical and Molecular formula for the following compound; 39.10% carbon, 7.67% hydrogen, 26.11% oxygen, 16.82% phosphorus, and 10.30% fluorine. (The molar mass of the compound would be 186 g/mol).

2. 15 grams of copper (II) chloride react with 20 grams of sodium nitrate produced 11.3 g of sodium chloride, then what is the theoretical yield and percent yield of this reaction?

3. Draw the crystal field splitting diagram for the following complexes.

   (i) $[Fe(CN)_6]^{3-}$

   (ii) $[NiCl_4]^{2-}$

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4. Give the nomenclature of following coordination compounds

   i. $[Co(en)_3]Cl_2$:

   ii. $Na[PtCl_3(NH_3)]$:

5 The equilibrium concentrations for the reaction between carbon monoxide and molecular chlorine to form $COCl_2$ (g) at 74 °C are $[CO] = 0.012$ M, $[Cl_2] = 0.054$ M, and $[COCl_2] = 0.14$ M. Calculate the equilibrium constants Kc and Kp.

6. A buffer is made by adding 0.300 mol CH_3COOH and 0.300 mol CH_3COONa to enough water to make 1.00 L of solution. The pK_a of the buffer is 4.74. Calculate the pH of this solution after 0.020 mol of NaOH is added

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7. In a test of a new reference electrode, a chemist constructs a voltaic cell consisting of a $Zn|Zn^{2+}$ half-cell (-0.76 V) and an $H_2|H^+$ half-cell under the following conditions: $[Zn^{2+}] = 0.010$ M $[H^+] = 2.5$ M $P_{H_2} = 0.30$ atm, calculate the E_{cell} at 298 K.

8. Given the following information:

$2\,NO(g) + O_2(g) \rightarrow 2\,NO_2(g)$ $\Delta H^\circ = -173$ kJ

$2\,N_2(g) + 5\,O_2(g) + 2\,H_2O(l) \rightarrow 4\,HNO_3(aq)$ $\Delta H^\circ = -255$ kJ

$N_2(g) + O_2(g) \rightarrow 2\,NO(g)$ $\Delta H^\circ = +181$ kJ

Calculate the ΔH° for the balanced reaction of $NO_2(g) + H_2O(l) \rightarrow HNO_3(aq) + NO(g)$.

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Answers

1. a 2. b 3. a 4. b 5. b 6. c
7. c 8. $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$ outermost shell electrons = 2+2 = 4 answer C

9. a 10. Bond order of O_2, F_2, N_2 ....

⇒ For O_2, total number of e^-s = 8+8 = 16

$= \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \{\pi 2p_y^2, \{\pi 2p_z^2, \{\pi^* 2p_y^1, \{\pi^* 2p_z^1$

Bond order = $\frac{\text{no of bonding } e^-\text{s} - \text{no of antibonding } e^-\text{s}}{2}$

$= \frac{10-6}{2} = \frac{4}{2} = \underline{\underline{2}}$

⇒ For F_2, Bond order = $\frac{10-8}{2} = \frac{2}{2} = \underline{\underline{1}}$

⇒ For N_2, Bond order = $\frac{10-4}{2} = \frac{6}{2} = \underline{\underline{3}}$

Bond order = 2, 1, 3 Answer C

11. H, 1s orbital + Be, P orbital → s-p overlap (axial)

Answer C

12. To answer this question, we shall consider the electron configuration of the central atom (metal). The ligands like F^-, Cl^-, H_2O, NH_3, CN^-, I^- ... have lone pairs of electrons and needs the empty orbitals of the central metal atom (ion).

Examples: i) $[Ni(CN)_5]^{3-}$, the central ion is Ni^{2+}

$Ni = 28e^-s \rightarrow [Ar]\ 4s^2\ 3d^8$; $Ni^{2+} = [Ar]\ 4s^0 3d^8\ 4p^0$

Ni^{2+} = $4s^0$ | $3d^8$ | $4p^0$

There are 5 ligands (CN^-) needs 5 empty orbitals. So that one s, one d and three p orbitals are used. The hybridization is sp^3d or dsp^3. The geometry is square pyramidal

10

13 b 14. a 15. a
16. d 17. c 18. a
19. b 20. a 21. a
22. a

23. $A + 2B \rightleftarrows C$
$[A] = 0.006M$, $[B] = 0.12M$, $[C] = 0.216M$
$Kc = \frac{[C]}{[A][B]^2} = \frac{0.216}{(0.006)(0.12)^2} = \frac{0.216}{864 \times 10^{-5}} = 2,500$
Answer ——

25. b
26. d, because there are equal moles of gaseous reactants and products.
27. Sodium acetate, CH_3COONa is added to the acid CH_3COOH. CH_3COONa reacts with water. $CH_3COO_{(aq)} + H_2O_{(l)} \rightleftarrows CH_3COOH + OH^-$
we can see that, a stronger base OH^- is produced. As a result, the pH value increases.
Answer b.

28. $pH = -\log[H^+] \Rightarrow 5 = -\log[H^+]$
$[H^+] = 10^{-5}$; For pH: 2; $pH: 2 = -\log[H^+]$
$[H^+] = 10^{-2}$ comparing 10^{-5} with 10^{-2}
$\frac{10^{-2}}{10^{-3}} = 10^3$ Answer b.

29. ΔH_f° HF = -161 kJ ; ΔH_f° HCl = -92 kJ
For exothermic processes, the larger the ΔH_f° value, the more stable the product formed.
Answer c.

30. $CaF_2(s) \rightarrow Ca^{2+}(aq) + 2F^-(aq)$; $K_{sp} = 3.2\times10^{-11}$

$x \qquad 2x$

$K_{sp} = (x)(2x) = 3.2\times10^{-11} = (x)(2x)^2$

$4x^3 = 3.2\times10^{-11} \Rightarrow x^3 = \frac{3.2\times10^{-11}}{4} = 8\times10^{-12}$

$x = \sqrt[3]{8\times10^{-12}} = 2.0\times10^{-4}$ mol/L ; Answer a.

31. $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$, Answer b.

32. Zn^{2+}/Zn and Ag^+/Ag

$Zn^{2+}/Zn = -0.763$ V ; $Ag^+/Ag = +0.799$ V

Oxidation: $Zn \rightarrow Zn^{2+} + 2e^-$, $E^\circ_{ox} = -(-0.763) = 0.763$ V

Reduction: $2Ag^+ + 2e^- \rightarrow 2Ag$, $E^\circ_{red} = +0.799$ V

$E^\circ_{cell} = E^\circ_{red} + E^\circ_{ox} = 0.799\text{V} + 0.763\text{V} = 1.562$ V

Answer a.

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34. During electrolysis cations (+ve) ions migrate to the cathode. Answer a.

35 E°_{red}: Mg < Al < Zn < Cu < Ag

$Cu \rightarrow Cu^{2+} + 2e^-$

$2Ag^+ + 2e^- \rightarrow Ag$ Answer C.

36. C

37. $HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$

1 mole 1 mole

$(V_1M_1)_{acid} = (V_2M_2)_{base}$

$M_1 = \frac{V_2M_2}{V_1} = \frac{15 \times 0.15}{22.5} = 0.1M$

$pH = -\log 0.1 = 1$ Answer b

38. a 39. 40. b

PART II Work-out

1. Given: C = 39.10 %, H = 7.67 %, O = 26.11 %
P = 16.82 %, F = 10.30 % & molar mass 184 g/mol
Empirical formula = ?

First calculate the % to atomic mass ratio:

$C = \frac{39.10}{12} = 3.26$; $H = \frac{7.67}{1} = 7.67$; $O = \frac{26.11}{16} = 1.63$

$P = \frac{16.82}{31} = 0.54$; $F = \frac{10.3}{19} = 0.57$

Next, divide the ratio by the smallest number

$C = \frac{3.26}{0.54} \simeq 6$; $H = \frac{7.67}{0.54} = 14$; $O = \frac{1.63}{0.54} = 3$

$P = \frac{0.54}{0.54} = 1$; $F = \frac{0.57}{0.54} \simeq 1$

∴ Empirical formula = $C_6H_{14}O_3PF$

2. $CuCl_2 + 2NaNO_3 \rightarrow 2NaCl + Cu(NO_3)_2$

135 gm 170 gm 118 gm

First calculate the limiting reagent from the balanced equation, $\frac{CuCl_2}{NaNO_3} = \frac{135}{170} = \frac{0.794}{1}$

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Using the given values $\frac{CuCl_2}{NaNO_3} = \frac{15}{20} = \frac{0.75}{1}$

Comparing the ratios, the limiting reagent is $CuCl_2$ with given mass 15 gm

135 gm of $CuCl_2$ = 118 gm of NaCl

15 gm of $CuCl_2$ = ?

$\frac{15}{135} \times 118 = 13.11$ gm of NaCl is produced and this is theoretical yield.

% yield = $\frac{\text{actual mass}}{\text{theoretical mass}} \times 100 = \frac{11.3}{13.1} \times 100 = 86.14\%$

4. (i) $[Co(en)_3]Cl_3$ tris(ethylenediamine)cobalt(II) chloride.

(ii) $Na[PtCl_3(NH_3)]$
Sodium monoamine chloroplatinium(II).

5. $CO + Cl_2 \rightleftharpoons COCl_2$ at 74 °c = 347 K

$K_c = \frac{[COCl_2]}{[CO][Cl_2]} = \frac{0.14}{0.012 \times 0.054} = 216$

$K_p = K_c(RT)^{\Delta n} = 216\left(8.31\ J/mol\ K \times 347\ K\right)^{(1-2)}$

$K_p = (6.22 \times 86)^{-1} = 216(2883.6)^{-1} = 7.5 \times 10^{-2}$

6. Given: a buffer solution containing 0.300 mol of CH_3COOH; 0.300 mol of CH_3COONa in 1 liter of solution pka = 4.74. Calculate the pH after 0.020 mol of NaOH is added.

First, pH before addition of NaOH.

$pH = pka + \log\frac{[base]}{[acid]} = 4.74 + \log\frac{0.300}{0.300} = 4.74$

After addition of 0.020 mol of NaOH; the base reacts with the acid (CH_3COOH)

$CH_3COOH_{(aq)} + OH^-_{(aq)} \rightarrow CH_3COO^-_{(aq)} + H_2O_{(l)}$

	1 mol	1 mol	1 mol
before	0.300 mol	—	0.300 mol
after:	0.300 − 0.020	0.020	0.300 + 0.020
equilibr.	0.28		0.320

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$pH = pKa + \log \frac{[Salt]}{[Acid]} = 4.74 + \log\left(\frac{0.220}{0.25}\right) = 4.70$

The results shows that due to the addition of the strong base, there is a slight increase of pH value (from 4.74 to 4.70) and this is the characteristics of buffer solutions

7. Given: Zn/Zn^{2+}, $E^\circ_{red} = -0.76V$; H_2/H^+ - $E^\circ_{red} = 0V$
$[Zn^{2+}] = 0.010\,M$; $[H^+] = 2.5\,M$; $P_{H_2} = 0.30\,atm$
E_{cell} at 298K - ?

$$E_{cell} = E^\circ_{cell} - RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b} = E^\circ_{cell} - \frac{RT}{nF} \ln Q$$

$$= E^\circ_{cell} - \frac{(8.31)(298)}{n(96485)} \ln Q$$

$$= E^\circ_{cell} - \frac{(0.0257)(2.303)}{n} \log Q$$

$$= E^\circ_{cell} - \frac{0.0592}{n} \log Q$$; considering cell rxn:

Anode: $Zn \longrightarrow Zn^{2+} + 2e^-$, $E^\circ_{ox} = -(-0.76) = 0.76V$
cathode: $2H^+ + 2e^- \rightarrow H_2$, $E^\circ_{red} = 0.00V$
$E^\circ_{cell} = E^\circ_{red} + E^\circ_{ox} = 0.00V + 0.76V = 0.76V$

$$E_{cell} = 0.76V - \frac{0.0592}{2} \log \frac{[Zn^{2+}]}{[H^+]^2}$$

$$= 0.76V - \frac{0.0592}{2} \log \frac{0.010}{(2.5)^2}$$

$$= 0.76V - \frac{0.0592}{2} \times (-2.80) = 0.76 + 0.083 = 0.843V$$

8. $2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$ $\Delta H^\circ = -173\,kJ$ ... (1)
$2N_{2(g)} + 5O_{2(g)} + 2H_2O_{(l)} \rightarrow 4HNO_{3(aq)}$ $\Delta H^\circ = -255\,kJ$ ... (2)
$N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)}$ $\Delta H^\circ = +181\,kJ$ ... (3)

Calculate ΔH° for $NO_{2(g)} + H_2O_{(l)} \rightarrow HNO_{3(aq)} + NO_{(g)}$
First rearrange equations (1), (2) & (3) so that upon addition they will give the final equation. Reverse equations (1) and (3)

$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$ $\Delta H^\circ = +173\,KJ$ ①

$2N_2(g) + 5O_2(g) + 2H_2O(l) \rightarrow 4HNO_3$ $\Delta H^\circ = -255\,KJ$ ②

$2NO(g) \rightarrow 2N_2(g) + O_2(g)$ $\Delta H^\circ = -181\,KJ$ ③

Now, multiply equation ①, ② & ③ by numbers such that when we add the equations it will give a balanced net equation. As a result, multiply equation ① by 3, equation ② by 1 and equation ③ by 2.

$3(2NO_2 \rightarrow 2NO + O_2$ $\Delta H^\circ = +173\,KJ)$

$1(2N_2 + 5O_2 + 2H_2O \rightarrow 4HNO_3$ $\Delta H^\circ = -255\,KJ)$

$2(2NO \rightarrow N_2 + O_2$ $\Delta H^\circ = -181\,KJ)$

$6NO_2 \rightarrow 6NO + 3O_2$ $\Delta H^\circ = +519\,KJ$

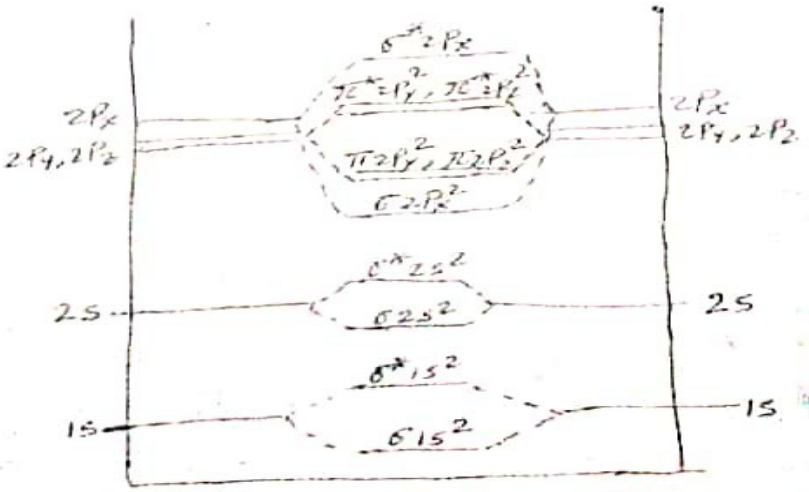
$2N_2 + 5O_2 + 2H_2O \rightarrow 4HNO_3$ $\Delta H^\circ = -255\,KJ$

$4NO \rightarrow 2N_2 + 2O_2$ $\Delta H^\circ = -362\,KJ$

$6NO_2 + 2H_2O \rightarrow 4HNO_3 + 2NO$ $\Delta H^\circ = -98\,KJ$

$\therefore \Delta H^\circ$ for the balanced rxn is $-98\,KJ$

9. For F_2 molecule which is homonuclear diatomic
a) draw MO energy diagram



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b) Calculate bond order for F_2^+ and F_2^-

⇒ For F_2^+, total no of e's: 9+9−1: 17

$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \begin{cases} \pi 2p_y^2 \\ \pi 2p_z^2 \end{cases}, \begin{cases} \pi^* 2p_y^2 \\ \pi^* 2p_z^1 \end{cases}$

Bond order: $\frac{1}{2}$ (No. of Bonding $\bar{e}$s − no of antibonding)

$= \frac{1}{2}(10-7) = \frac{1}{2}(3) = \underline{\underline{3/2}}$

⇒ For F_2^-, total no of e's: 9+9+1: $\underline{\underline{19}}$

Bond order: $\frac{1}{2}(10-9) = \frac{1}{2}(1) = \underline{\underline{1/2}}$

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