Problem Set #13

CHEM101A: General College Chemistry

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22 Topic F Problem 22

Draw pictures showing how each of the following MOs is formed by combining the specified atomic orbitals. Include the signs of the lobes for each atomic orbital.

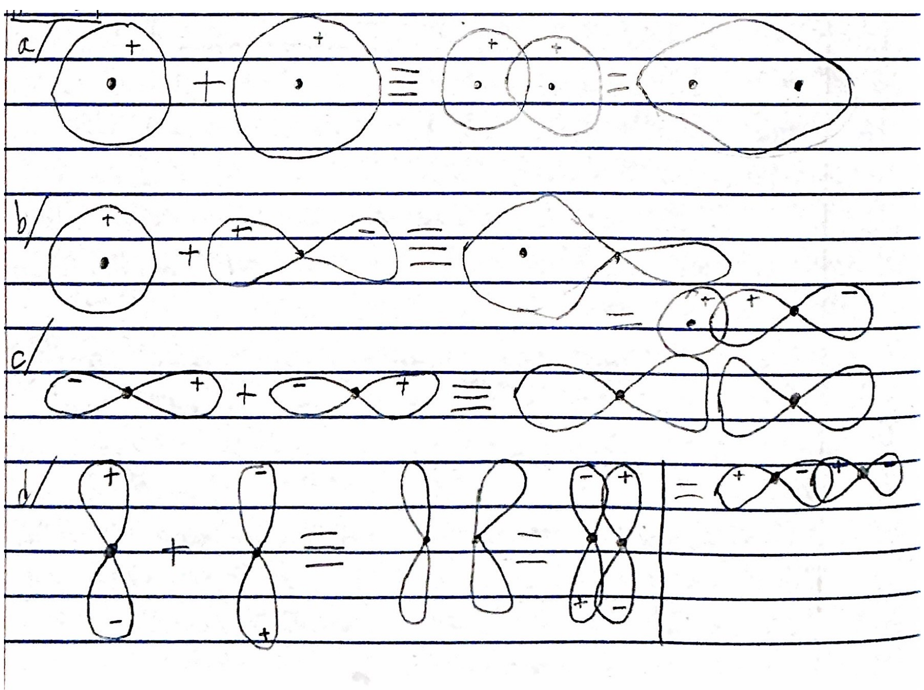
a) a sigma bonding MO that is formed by two 2s orbitals

b) a sigma bonding MO that is formed by a 1s orbital and a 2p orbital

c) a sigma antibonding MO that is formed by two 2p orbitals

d) a pi antibonding MO that is formed by two 2p orbitals

22.1 Solution



23 Topic F Problem 23

A d orbital and a p orbital can combine to form molecular orbitals in several different ways. Draw a picture of the overlap between these two atomic orbitals that would produce each of the following molecular orbitals. Include the signs of the lobes for each atomic orbital.

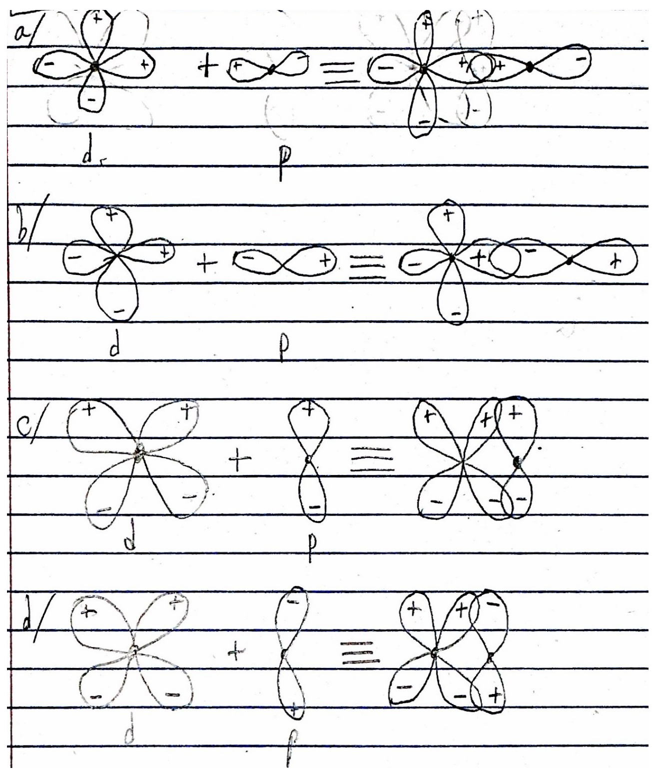
a) a sigma bonding MO

b) a sigma antibonding MO

c) a pi bonding MO

d) a pi antibonding MO

23.1 Solution



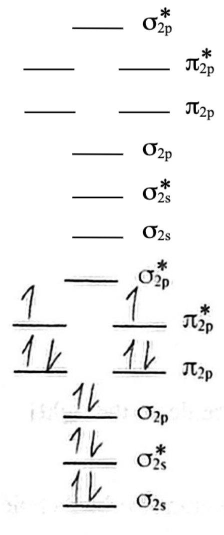
24 Topic F Problem 24

The molecular orbital energy diagram for the valence orbitals of the NO^- ion is shown below. Use this diagram to answer the following questions.

a) What is the bond order in NO^-?

b) Is NO^- diamagnetic, or is it paramagnetic? How can you tell?

c) Which has the larger bond distance, NO^- or NO? Assume that this energy diagram also applies to NO.



24.1 Solution (a)

Add up the bonding electrons and subtract the antibonding electrons. Then divide the result by two. The bond order is the quotient.

$$\frac{8-4}{2} = \frac{4}{2} = \boxed{2} \tag{1}$$

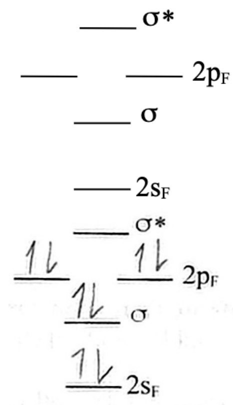
24.2 Solution (b)

There are empty bond orbitals (both π^*_{2p}). This means that the NO^- as a molecule is paramagnetic.

24.3 Solution (c)

If we look at the diagram for NO, the only difference is one fewer electron in π^*_{2p}. This raises the bond order to 2.5. That in turn corresponds to a smaller bond distance. This means that $\boxed{NO^-}$ has the larger bond distance.

25 Topic F Problem 25



The molecular orbital energy diagram for the valence orbitals of HF is shown below. Use this diagram to answer the following questions. Note that the orbitals labeled $2s_F$ and $2p_F$ are nonbonding orbitals on the fluorine atom; electrons in these orbitals do not affect the bond order.

a) Based on this diagram, what is the bond order in HF?

b) Is HF diamagnetic, or is it paramagnetic? How can you tell?

c) How many nonbonding electrons are there in HF?

d) Draw a picture that shows how the σ orbital is formed from atomic orbitals on hydrogen and fluorine.

e) If an electron were removed from the HF molecule, how would the bond energy be affected?

25.1 Solution

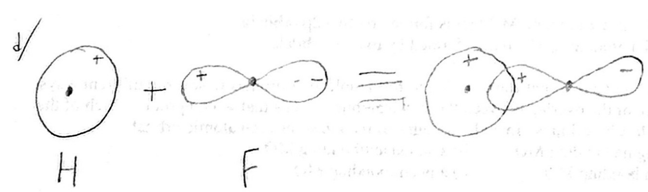
a/ One ($\frac{2-0}{2}$). We ignore the 2s and 2p orbitals' electrons because they are nonbonding.

b/ Diamagnetic. There are no unpaired electrons.

c/ Six, all those contained in the 2s and 2p orbitals.

d/ See below. Bonds not drawn to scale.

e/ The electron would come out of the 2p orbital from the Fluorine. As such, it would have no effect.



1 Topic G Problem 1

List the defining characteristics of a dynamic equilibrium as described in the video.

1.1 Solution

Reactions are performed in both directions. There remains (roughly) a constant amount (or concentration) of each chemical at every point. The rate of reaction is equal to the rate of reverse reaction.

2 Topic G Problem 2

a) The formation and decomposition ammonium chloride is provided as an example of a reversible chemical reaction. Describe the characteristics required of an experimental set-up in order to establish a dynamic chemical equilibrium.

b) Write the equation representing the chemical equilibrium for the system of ammonium chloride, ammonia, and hydrogen chloride.

2.1 Solution

3 Topic G Problem 3

a) What is a heterogeneous chemical equilibrium? Search the internet to find an example of a heterogeneous chemical equilibrium system (other than the one in the video.) Write the equilibrium equation for your example.

b) What is a homogenous chemical equilibrium? Search the internet to find an example of a homogeneous equilibrium system. Write the equilibrium equation for your example.

3.1 Solution

4 Topic G Problem 4

How can you tell from a graph of reaction rate vs. time when a system has established chemical equilibrium? (What is true for the rate of the forward reaction and the rate of the reverse reaction at equilibrium?)

4.1 Solution

5 Topic G Problem 5

How can you tell from a graph of concentrations vs. time when a system has established chemical equilibrium? (What is true for the concentrations of the products and the concentrations of the reactants at equilibrium?)

5.1 Solution

6 Topic G Problem 6

For the reaction below, the equilibrium constant K is greater than 1.

$$\text{fructose} \rightleftharpoons \text{glucose} \quad K >> 1$$

If a solution initially contains equal concentrations of fructose and glucose, which of the following statements must be true at that initial moment? Explain your answer.

a) The forward reaction (fructose $\rightarrow$ glucose) is faster than the reverse reaction.

b) The reverse reaction is faster than the forward reaction.

c) The forward and reverse reactions have equal rates.

6.1 Solution

(a) would be the only one true. Since K > 1, that means that by equilibrium, there will be more glucose than frucose. If we start with an equal amount of each, there would be more glucose being produced than fructose so as to approach the equilibrium. That means that the reaction to create glucose (the forward reaction) will occur more (or be faster) than the reverse reaction.

7 Topic G Problem 7

Write the K_c expressions for each of the following reactions. Note: the subscript "c" tells you that this is the equilibrium constant in terms of concentrations (mol/L).

a) $2\,NO(g) + O_2(g) \longleftrightarrow 2\,NO_2(g)$

b) $4\,Ag(s) + O_2(g) \longleftrightarrow 2\,Ag_2O(s)$

c) $CaCO_3(s) + CO_2(aq) + H_2O(l) \longleftrightarrow Ca_2{}^{+}(aq) + 2\,HCO_3{}^{-}(aq)$

7.1 Solution (a)

$$\mathrm{K_c} = \frac{[\mathrm{NO_2}]^2}{[\mathrm{NO}]^2[\mathrm{O_2}]} \tag{2}$$

7.2 Solution (b)

$$\mathrm{K_c} = \frac{[\mathrm{Ag_2O}]^2}{[\mathrm{Ag}]^4[\mathrm{O_2}]} = \frac{1}{[\mathrm{O_2}]}$$

7.3 Solution (c)

$$\mathrm{K_c} = \frac{[\mathrm{Ca_2}^{+}][\mathrm{HCO_3}^{-}]^2}{[\mathrm{CaCO_3}][\mathrm{CO_2}][\mathrm{H_2O}]} = \frac{[\mathrm{Ca_2}^{+}][\mathrm{HCO_3}^{-}]^2}{[\mathrm{CO_2}]}$$

8 Topic G Problem 8

a) Write the K_p expressions for reactions a and b in the previous problem. Note: the subscript "p" tells you that this is the equilibrium constant in terms of partial pressures (atm).

b) If the value of K_c for reaction (a) in the previous is 2.8×10^{11} at 200°C, what is the value of K_p at this temperature?

8.1 Solution (a)

This is similar to the last problem, but you use pressures rather than only consider gases.
a/

$$\mathrm{K_p} = \frac{\mathrm{P}^2_{\mathrm{NO_2}}}{\mathrm{P}^2_{\mathrm{NO}}\mathrm{P}_{\mathrm{O_2}}} \tag{3}$$

b/

$$\mathrm{K_p} = \frac{1}{\mathrm{P}_{\mathrm{O_2}}} \tag{4}$$

8.2 Solution (b)

This is solvable using an equation for $\mathrm{K_p}$ from $\mathrm{K_c}$.

$$\mathrm{K_p} = \mathrm{K_c}(\mathrm{RT})^{\Delta \mathrm{n}} \tag{5}$$

We have values for $\mathrm{K_c}$, R (the value involving atmospheres), and T. Our value for Δn (change in number of gaseous moles) will be -1 since the only gas is O_2, which we lose a mole of.

$$\mathrm{K_p} = K_c(RT)^{\Delta n} = 2.8 \times 10^{11}\,\frac{\mathrm{L}}{\mathrm{mol}}\left(0.08206\,\frac{\mathrm{atm \cdot L}}{\mathrm{mol \cdot K}} \times 473.15\mathrm{K}\right)^{-1} \tag{6}$$

$$= 7.212 \times 10^9\,\frac{1}{\mathrm{atm}} = \boxed{7.2 \times 10^9\,\frac{1}{\mathrm{atm}}} \tag{7}$$

9 Topic G Problem 9

For the reaction below, $K_c = 6.17$ at a certain temperature.

$$PCl_3(g) + Cl_2(g) \longleftrightarrow PCl_5(g)$$

Determine whether each of the following mixtures is at equilibrium. Assume that each mixture is at the same temperature as that for the provided K_c. For each mixture that is not at equilibrium, tell whether the reaction will go forward or backward.

a) A mixture in which the concentration of PCl_3 is 0.0381 M, the concentration of Cl_2 is 0.0593 M, and the concentration of PCl_5 is 0.0139 M.

b) A mixture in which the concentration of PCl_3 is 0.0482 M, the concentration of Cl_2 is 0.289 M, and the concentration of PCl_5 is 0.0455 M.

c) A mixture that contains PCl_3 and PCl_5, but no Cl_2.

d) A mixture that contains 0.21 mol of PCl_3, 0.48 mol of Cl_2, and 0.39 mol of PCl_5 in an 8.00 L container.

9.1 Solution (a)

All of these will involve calculating Q, which depends on concentrations, each of which would be calculatable by dividing moles by volume when applicable.

$$Q = \frac{[PCl_5]}{[PCl_3][Cl_2]} = \frac{0.0139}{0.0593 \times 0.0381} = 6.15 \tag{8}$$

This is likely at equilibrium. Measurements may be a little off. If this is indeed the value of Q at this point, the reaction would be going forward.

9.2 Solution (b)

$$Q = \frac{0.0455}{0.0482 \times 0.289} = 3.27 \tag{9}$$

This reaction will definitely be going forwards.

9.3 Solution (c)

Well, here $[Cl_2]$ will be zero, so Q will be ∞. What a way to involve calculus in Chemistry. In any case, ∞ is greater than 6.17, so the reaction will occur in reverse.

9.4 Solution (d)

$$Q = \frac{\frac{n_{\mathrm{PCl_5}}}{V}}{\frac{n_{\mathrm{PCl_3}}}{V} \times \frac{n_{\mathrm{Cl_2}}}{V}} = V \times \frac{n_{\mathrm{PCl_5}}}{n_{\mathrm{PCl_3}} \times n_{\mathrm{Cl_2}}} \tag{10}$$

$$= 8.00 \times \frac{0.39}{0.21 \times 0.48} = 31.0 \tag{11}$$

The reaction will be going in reverse.

10 Topic G Problem 10

If Q, the reaction quotient, is greater than K for a reaction mixture, which of the following will happen?

a) The reaction will go in the direction that increases Q.

b) The reaction will go in the direction that decreases Q.

c) The reaction will go in the direction that increases K.

d) The reaction will go in the direction that decreases K.

10.1 Solution

Statement (b) is correct. K does not change during a reaction (although chemical quantities and temperature changes may change it). Q will always try to approach K, so if Q is greater than K, Q will attempt to decrease.

11 Topic G Problem 11

For the reaction $N_2(g) + 3\,H_2(g) \longleftrightarrow 2\,NH_3(g)$, $K_p = 0.0489$ at 256°C. For parts a through d, assume that the reaction is at this temperature.

a) An equilibrium mixture contains 0.100 atm of N_2 and 0.200 atm of H_2. What is the partial pressure of NH_3 in this mixture?

b) A second equilibrium mixture contains 830 torr of H_2 and 42 torr of NH_3. What is the partial pressure of N_2 in this mixture?

c) A third equilibrium mixture contains 0.0100 mol/L of N_2 and 0.0300 mol/L of NH_3. What is the concentration of H_2 in this mixture?

d) A fourth equilibrium mixture contains equal concentrations of all three chemicals. What is the pressure of each substance in this mixture?

11.1 Solution (a)

For all of this, we will be using an equation for $\mathrm{K_p}$.

$$\mathrm{K_p} = \frac{\mathrm{P^2_{NH_3}}}{\mathrm{P_{N_2}P^3_{H_2}}} \tag{12}$$

Solve for $P_{\mathrm{NH_3}}$ and find the answer.

$$\mathrm{P_{NH_3}} = \sqrt{\mathrm{K_p P_{N_2} P^3_{H_2}}} = \sqrt{(0.0489)(0.100)(0.200)^3} = \boxed{0.00625\,\mathrm{atm}} \tag{13}$$

11.2 Solution (b)

First convert from torr to atm.

$$P_{\mathrm{H_2}} = 830\,\mathrm{torr} \times \frac{1\,\mathrm{atm}}{760\,\mathrm{torr}} = 1.092\,\mathrm{atm} \tag{14}$$

$$P_{\mathrm{NH_3}} = 42\,\mathrm{torr} \times \frac{1\,\mathrm{atm}}{760\,\mathrm{torr}} = 0.05526\,\mathrm{atm} \tag{15}$$

Now we solve for N_2.

$$P_{\mathrm{N_2}} = \frac{P^2_{\mathrm{NH_3}}}{K_p P^3_{\mathrm{H_2}}} = \frac{0.05526^2}{0.0489 \times 1.092^3} = \boxed{0.048\,\mathrm{torr}} \tag{16}$$

11.3 Solution (c)

First calculate K_c. Our value for Δn is -2. The temperature is Kelvin is 529.15 K.

$$\mathrm{K_c} = \frac{\mathrm{K_p}}{(0.08206 * 529.15)^{-2}} = \frac{0.0489}{(0.08206 * 529.15)^{-2}} = \underline{92.1}997 \tag{17}$$

From here, find the concentration of H_2.

$$[\mathrm{H_2}] = \sqrt[3]{\frac{[\mathrm{NH_3}]^2}{K_c \times [\mathrm{N_2}]}} = \sqrt[3]{\frac{0.0300^2}{\underline{92.1}997 \times 0.0100}} = \boxed{0.0992\,\mathrm{M}} \tag{18}$$

11.4 Solution (d)

Suppose that we had a concentration of c of each substance. We can form an equation for $\mathrm{K_c}$ of each and use that to find what K_p would be in this instance, then solve for c.

$$\mathrm{K_c} = \frac{\mathrm{c}^2}{\mathrm{c} \times \mathrm{c}^3} = \mathrm{c}^{-2} \tag{19}$$

$$K_c = \frac{K_p}{(RT)^{\Delta n}} = c^{-2} \tag{20}$$

$$c = \sqrt{\frac{(RT)^{\Delta n}}{K_p}} = \sqrt{\frac{(0.08206 * 529.15)^{-2}}{0.0489}} = 0.\underline{104}144\,\mathrm{M} \tag{21}$$

This can be used alongside the ideal gas law to find the pressure of all of them, which would be identical. Bear in mind that $\mathrm{c} = \frac{\mathrm{n}}{\mathrm{V}}$.

$$P = \frac{n}{V}RT = cRT \tag{22}$$

$$= 0.\underline{104}144\,\mathrm{M} \times 0.08206 \times 529.15 = \boxed{4.52\,\mathrm{atm}} \tag{23}$$

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