2017CS10328 ANKIT KUMAR SINGH

CML100 Minor 2 Oct. 06, 2017 Time: 60 min

Use of electronic gadgets, other than calculators, during the exam is prohibited.

Inorganic Chemistry

1. From the reaction of $NiBr_2$ and Ph_2EtP, it is possible to isolate green crystals of $[Ni(Ph_2EtP)_2Br_2]$, which has a magnetic moment of 3.2 BM, and red crystals of $[Ni(Ph_2EtP)_2Br_2]$, which has zero magnetic moment. When either of these is dissolved in dichloromethane at 40 °C, the resultant solution has a magnetic moment of 2.69 BM. Suggest structures for the green and red crystals. Explain the magnetic moment of the solution. (2+2)

2. $Ni(acac)_2$ is paramagnetic, but it is not tetrahedral. Suggest a structure consistent with these facts. (acac = $CH_3COCH_2COCH_3$) (3)

3. Which of the following two complexes have normal and/or inverse spinel structure? $CoFe_2O_4$, $NiFe_2O_4$. Explain why? (2+2)

4. With the help of the MO diagram of CO explain its bonding to a metal. (5)

5. Determine the total number of metal-metal bonds in $[\eta^5-CpMo(CO)_2]_2$ (Group 6: Cr, Mo, W). Show your reasoning. (4)

Physical Chemistry

6. Cold interstellar molecular clouds often contain the molecule cyanogen (CN), whose first rotational excited states have an energy of 4.7×10^{-4} eV above the ground state. There are actually three such excited states, all with the same energy. In 1941, studies of the absorption spectrum of starlight that passes through these molecular clouds showed that for every ten CN molecules that are in the ground state, approximately three others are in the three first excited states (that is, an average of one in each of these states). To account for this data, astronomers suggested that the molecules might be in thermal equilibrium with some "reservoir" at a well-defined temperature. What is that temperature? $k = 8.62 \times 10^{-5}$ eV K^{-1}. (3)

7. At non-zero temperatures, irregularities are produced in completely ordered atomic crystal lattices. One irregularity, a Schottky defect, arises when an atom moves from a lattice site to the surface leaving behind a vacancy. What is the entropy of an isolated monatomic crystalline solid of N atoms with n Schottky defects? (4)

8. Suppose you have 10 atoms of ceeemelium: 4 with energy 0 eV, 3 with energy 1 eV, 2 with energy 4 eV, and 1 with energy 6 eV. What is the average energy of the system? (3)

9. The effective nuclear charge is nearly equal to the nuclear charge for the 1s orbital but decreases rapidly for the outermost electron as the principal quantum number increases. True or false? Justify your answer. No justification, no credit! (2)

10. Give an example of an atomic orbital (AO) for which the overlap with another of its kind reaches its maximum value only as the internuclear separation approaches zero. Also give an example of an atomic orbital for which the overlap goes through a maximum value and then decreases as the internuclear separation approaches zero. Give your reasoning. (4)

11. A measure of the change in electron density due to bond formation (or lack of it) in a homonuclear diatomic molecule (AB) is to plot $\Delta = \psi^2_{MO} - \frac{1}{2}\psi^2_A - \frac{1}{2}\psi^2_B$. For H_2^+, sketch the bonding molecular orbital, ψ_b, and its Δ for H_2^+ IN THE SAME FIGURE. In another figure do the same for the anti-bonding molecular orbital, ψ_a, and its Δ (4)