## NIVERSITÀ DI PISA



## Concorso pubblico anno accademico 2019/2020 per l'accesso al Corso di dottorato in Scienze Chimiche e dei Materiali

(bandito con decreto rettorale n.43379 del 24 aprile 2019 e successive modifiche e integrazioni)

- 1. Discuss the energy level diagram of the molecular orbitals in a homonuclear diatomic molecule.
- 2. Describe the aspects of thermodynamic control and kinetic control of chemical reactions by referring to the case of two competing reactions that provide two different products B, C:

 $A \rightarrow B$  $d[A]/dt=-k_1[A]$  $K_1 = [B]_{eq}/[A]_{eq}$  $A \rightarrow C$  $d[A]/dt=-k_2[A]$  $\mathsf{K_2} {=} [\mathsf{C}]_{eq} / [\mathsf{A}]_{eq}$ 

and in which the relative kinetic constants and equilibrium constants are such that  $k_1 > k_2$  e  $K_1 < K_2$ .



- 3. Describe the Arrhenius equation for the dependence of kinetic constants on temperature and discuss the relative molecular interpretation.
- 4. Explain why the following reaction leads to the products that are shown

$$NH_2$$
  $NaNO_2$   $OH$  +

5. What is the direction of the dipole moment in fulvene and calicene? Which compound has the stronger dipole moment? Explain

6. In each of the following pairs, which compound is a stronger base? Why?

or 
$$NH_2$$
 or  $NH_2$  or  $NH_2$ 









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- 7. The role of catalyst in chemical reactions, with particular reference to activity, selectivity and productivity in industrial processes.
- 8. Composite materials: morpholgy and usual preparation methods, the properties induced or improved with respect to the pure matrix and main fields of application.
- 9. What differentiates a macromolecule from a low molecular weight compound?
- 10. Sodium hydride when dissolved in water produces:
  - 1. Acidic solution
  - 2. Basic solution
  - 3. Neutral solution
  - 4. Cannot be predicted
- 11. Give reason for the following in one or two sentences: "solid carbon dioxide is known as dry ice"
- 12. The experimental magnetic moments (Bohr magnetons) of a number of complex ions are listed.

Comment on (a) the d electron configuration and (b) the validity of the 'spin only' formula.

	Magnetic Moment
Ti(H <sub>2</sub> O) <sub>6</sub> <sup>3+</sup>	1.8
Mn(CN) <sub>6</sub> <sup>4-</sup>	2.2
Mn(H <sub>2</sub> O) <sub>6</sub> <sup>2+</sup>	5.9

- 13. How are the detection limit and the instrumental detection limit defined according to IUPAC? Explain the differences between these two concepts.
- 14. Describe the working principle and the main characteristics of either a gas or a liquid chromatographic detector.
- 15. When performing a spectrophotometric determination of a molecule, explain how the measurement wavelength is selected and why.







ALP.