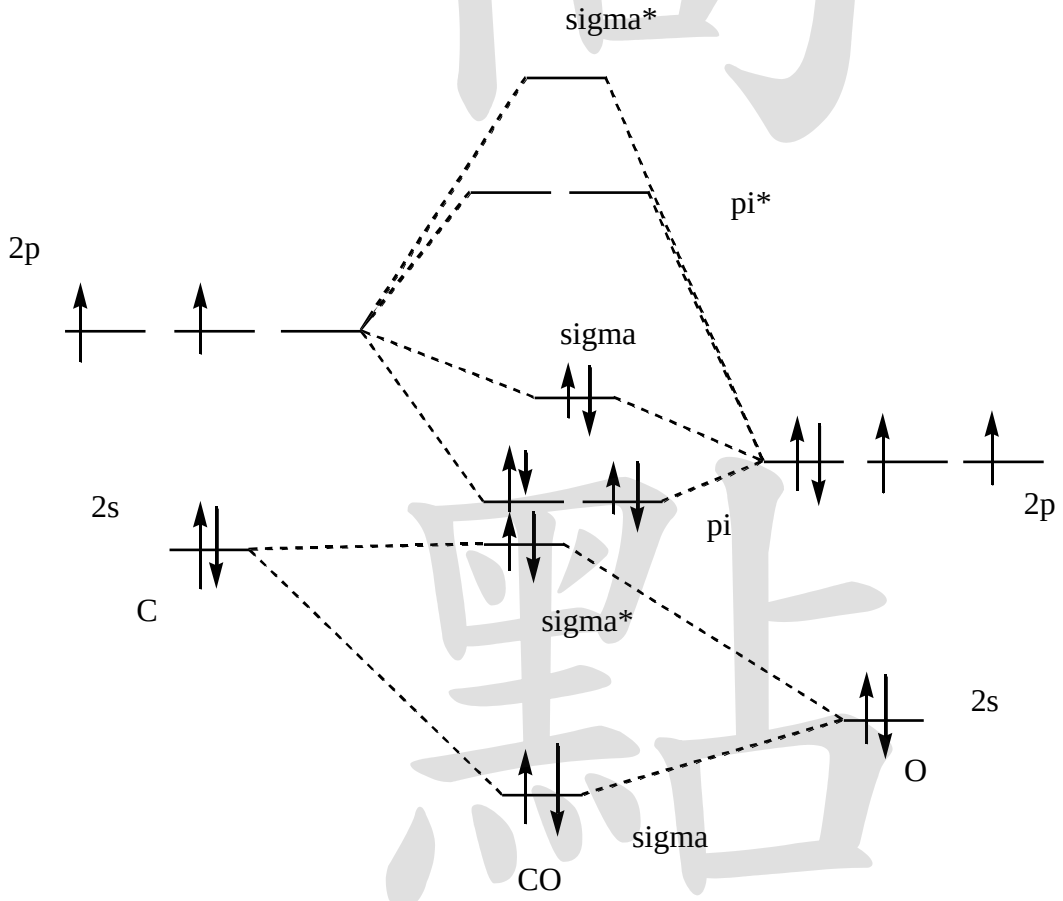
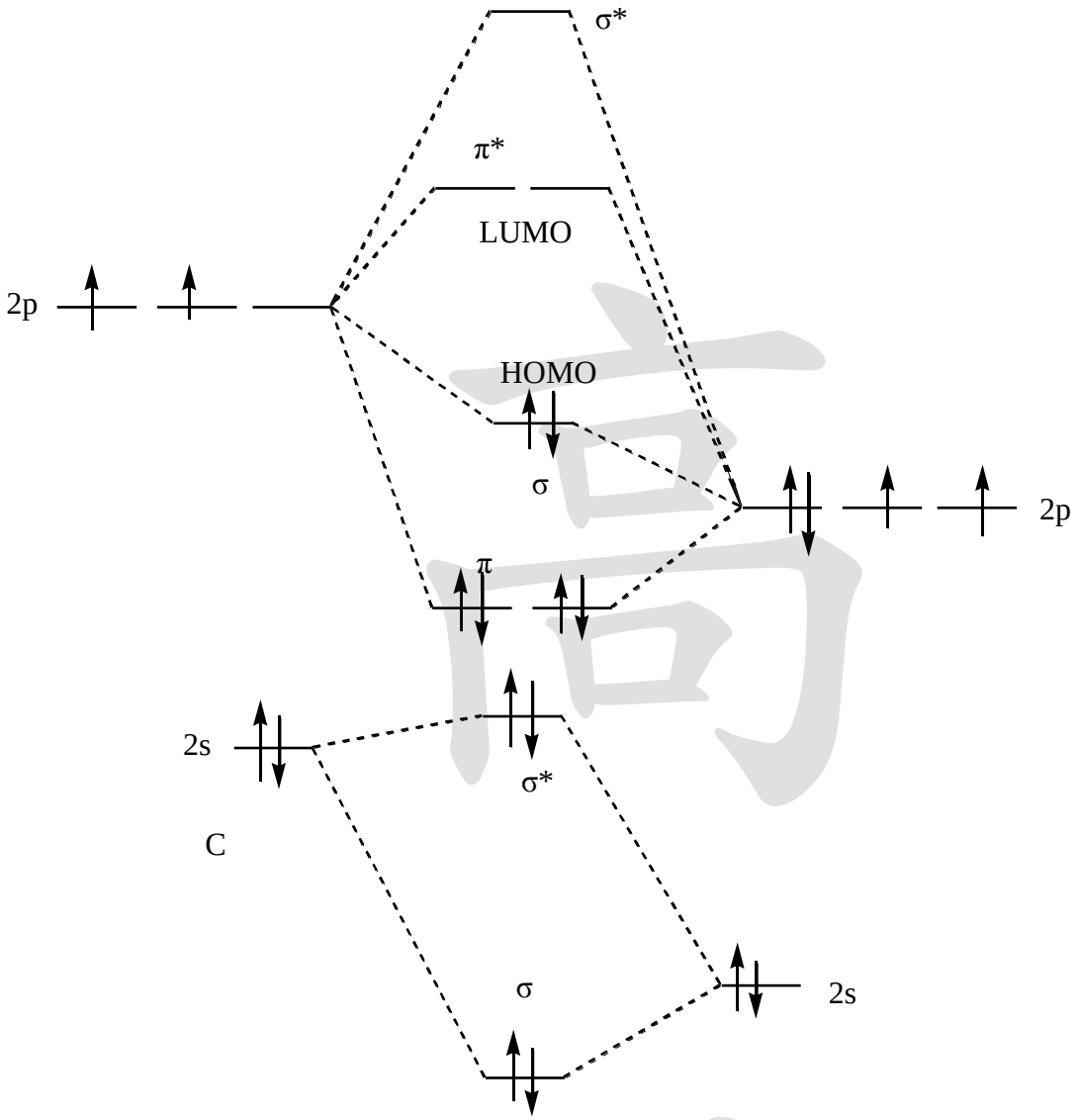
第 22 題:

Construct the molecular orbital (MO) diagram of carbon monoxide (CO) step-by-step: (A) put atomic orbitals (AO) of C atom on the left side and those of O atom on the right (including only 2s and 2p electrons, and note the relative energy of AOs of C and O atoms), (B) put up the MO of CO molecule in the middle, and connect the MOs with the contributing AOs. (C) Fill up the electrons of AOs and MOs. Note that when combining the p orbitals, the pi molecular orbital has a lower energy than the sigma molecular orbital

ANS:





普化講義第二冊, p.133

第 28 題:

The reaction between nitric oxide and hydrogen,

$2NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$

may proceed via the following mechanism:

$NO(g) + NO(g) \leftrightarrow N_2O_2(g)$ k_1/k_{-1}

$N_2O_2(g) + H_2(g) \leftrightarrow N_2O(g) + H_2O(g)$ k_2/k_{-2}

Give the rate law for the overall reaction if the second step is the rate-determining step

ANS:

$r = k_2[N_2O_2][H_2]$ because of the second step is rds

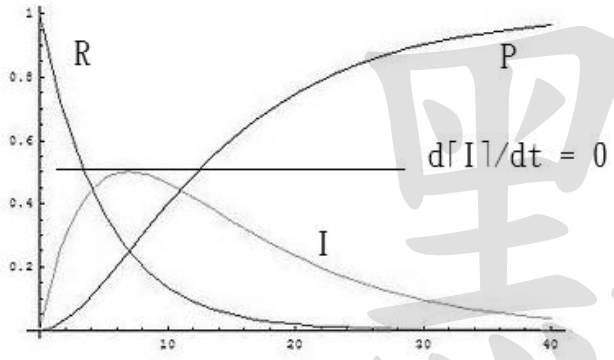
$K = k_1/k_{-1} = [N_2O_2]/[NO]^2$

$r = k_2K[NO]^2[H_2]$

****The Steady-State Approximation 穩態逼近法**

R → I → P , R: 反應物, I: 中間物, P：產物

利用中間物濃度變化極大值處切線斜率為零(一次微分等於零), 找出中間物與各物種間的函數關係 → 推出速率定律式(rate law)



$2NO_{(g)} + H_{2(g)} \rightarrow N_2O_{(g)} + H_2O_{(g)}$

$2NO \underset{k-1}{\overset{k1}{\rightleftharpoons}} N_2O_2$

$N_2O_2 + H_2 \xrightarrow{k2} N_2O + H_2O$

$d[N_2O_2]/dt = 0$ (中間體濃度對時間的變化率為零)

$k_1[NO]^2 - k_{-1}[N_2O_2] - k_2[N_2O_2][H_2] = 0$

because rate $= k_2[N_2O_2][H_2]$

so $[N_2O_2] = \dfrac{k_1[NO]^2}{k_{-1} + k_2[H_2]}$

rate $= \dfrac{k_2k_1[NO]^2[H_2]}{k_{-1} + k_2[H_2]}$

請按 $k_2[H_2] >> k_{-1}$ and $k_{-1} >> k_2[H_2]$等條件改變 rate law 的寫

普化講義第四冊, p.77