# Giochi della chimica nazionali 2008
## Soluzioni dei problemi a risposta aperta

**1.1** **Se metto qualche goccia di soda in alluminio si forma un precipitato bianco.**
**Se metto qualche goccia di alluminio in soda si forma un alone bianco che si ridiscioglie immediatamente.**

**1.2**

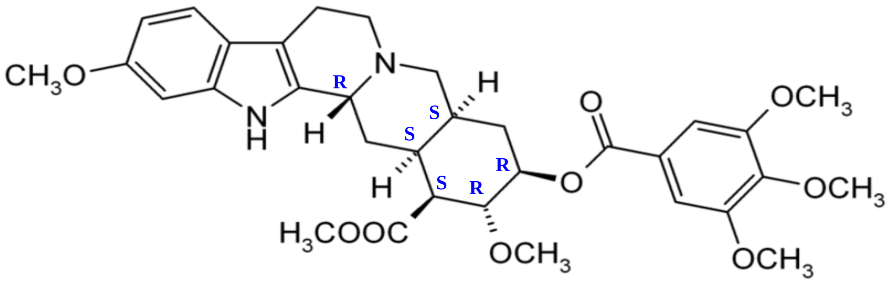
| Provetta 1 | Provetta 2 | Provetta 3 | Provetta 4 | Provetta 5 | Provetta 6 |
|---|---|---|---|---|---|
| $FeSO_4$ | $H_2SO_4$ | $Mn(NO_3)_2$ | $H_2O_2$ | $Pb(NO_3)_2$ | NaOH |

**1.3**
(1)+(4) $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^-$
(1)+(5) $SO_4^{2-} + Pb^{2+} \rightarrow PbSO_4$
(1)+(6) $Fe^{2+} + OH^- \rightarrow Fe(OH)_2$
$Fe(OH)_2 + O_2 + H_2O \rightarrow Fe(OH)_3$
(2)+(5) $Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4$
(3)+(6) $Mn^{2+}$ è $OH^- \rightarrow Mn(OH)_2$
$Mn(OH)_2 + O_2 \rightarrow MnMnO_3$
$Mn(OH)_2 + O_2 \rightarrow MnO_2$
(5)+(6) $Pb^{2+} + OH^- \rightarrow Pb(OH)_2$
$Pb(OH)_2 + OH^- \rightarrow Pb(OH)_4^{2-}$

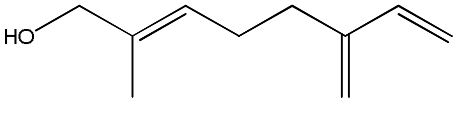
**1.4**
(1)+(2)+(4) $Fe^{2+} + H^+ + H_2O_2 \rightarrow Fe^{3+} + H_2O$
(1)+(4)+(6) $Fe^{2+} + H_2O_2 + OH^- \rightarrow Fe(OH)_3$
(3)+(4)+(6) $Mn^{2+} + H_2O_2 + OH^- \rightarrow MnO_2 + H_2O$

**2.1** **ci sono 6 stereocentri**

**2.2**

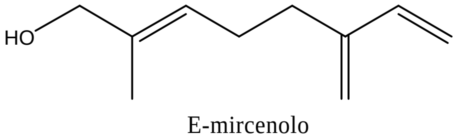



**3.1**



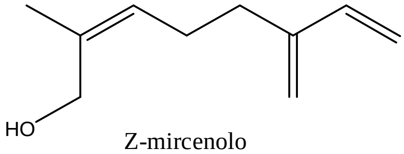

**3.2** **due possibili stereoisomeri (E e Z)**

**3.3**

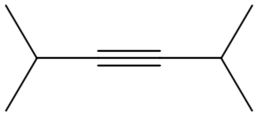


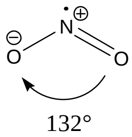
E-mircenolo

e

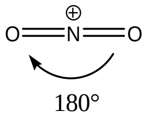


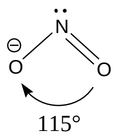
Z-mircenolo

**3.4** 



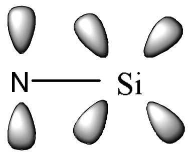

**4.1** **$NO_2$, geometria angolare**



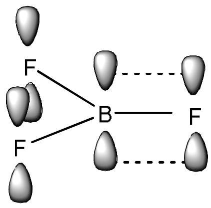




**4.2** **$NO_2^+$, lineare** **$NO_2^-$, angolare**

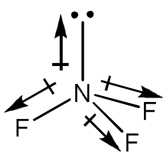
**4.3** **parziale carattere di doppio legame dei legami N-Si dovuta alla sovrapposizione tra l'orbitale p dell'azoto e gli orbitali d del silicio:**



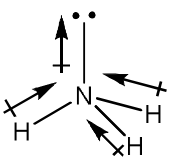

**4.4** **Nel $BF_3$ si ha una parziale sovrapposizione tra gli orbitali p vuoti del boro e gli orbitali p pieni del fluoro:**




**4.5** **$NH_3$ può formare legami a idrogeno, mentre $NF_3$ no.**
**L'elevata elettronegatività del fluoro rende il doppietto dell'azoto meno disponibile.**
**Nell'$NF_3$ il doppietto contribuisce al momento dipolare in direzione opposta rispetto ai dipoli N-F. mentre nell'ammoniaca è nella stessa direzione.**




e




**4.6** **$Na + NH_{3(l)} \rightarrow Na^+ + e^-_{(NH3)}$ blu**
**$Na + NH_{3(l)} + Fe^{2+}_{(cat)} \rightarrow Na^+ + NH_2^- + H_2$**

**5.1** **$\Delta S_{sis} > 0$** **$\Delta S_{amb} < 0$**
**5.2** **$\Delta S_{sis} = n\ R\ \ln(V_f/V_i)$** **$\Delta S_{sis} = 27.4\ J\ K^{-1}$**
**5.3** **$\Delta S_{amb} = -p_{ex}\Delta V/T$** **$\Delta S_{amb} = -6.9\ J\ K^{-1}$**
**5.4** **$\Delta S_{tot} = 20.5\ J\ K^{-1}$, rispetta la seconda legge della termodinamica.**
**5.5** **brinamento (gas → solido)**
**5.6** **condensazione (gas → liquido) e poi solidificazione (liquido → solido)**

**5.7** $\ln\left(\frac{P_2}{P_1}\right)=\frac{\Delta \bar{H}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$ $\Delta \bar{H} =$ **26.1 kJ mol$^{-1}$**

**5.8** **$\Delta H°$ = 172.5 kJ mol$^{-1}$**
**$\Delta S°$ = 176 J K$^{-1}$ mol$^{-1}$**
**$\Delta G°$ = 120 kJ mol$^{-1}$**
**$\Delta G°$ > 0 quindi K<1**

**5.9** **K = 1 → $\Delta G°$ = 0 → $\Delta H°$ = T$\Delta S°$**
**T = 980 K**

**6.1** $s = \sqrt[3]{\frac{K_{ps}}{4}} = 1.14 \cdot 10^{-5}\,\mathrm{M}$

**6.2** **$K_{ps} = x\,(x + 0.01)^2$ x << 0.01**
**$K_{ps} = x\,(0.01)^2$**
**x = $s$ = 5.9 10$^{-11}$ M**

**6.3** **$s$ = ½[OH$^-$] = c(Cd)**
**c(Cd) = $[Cd^{2+}] + [Cd(CN)^+] + [Cd(CN)_2] + [Cd(CN)_3^-] + [Cd(CN)_4^{2-}]$**
**½[OH$^-$] = $[Cd^{2+}]\,(1 + K_1[CN^-] + K_1K_2[CN^-]^2 + K_1K_2K_3[CN^-]^3 + K_1K_2K_3K_4[CN^-]^4)$**
**½[OH$^-$] = $\frac{K_{ps}}{[OH^-]^2}\,(1 + K_1[CN^-] + K_1K_2[CN^-]^2 + K_1K_2K_3[CN^-]^3 + K_1K_2K_3K_4[CN^-]^4)$**
**[OH$^-$] = $\sqrt[3]{2\cdot K_{ps}\cdot\left(1 + K_1[CN^-] + K_1K_2[CN^-]^2 + K_1K_2K_3[CN^-]^3 + K_1K_2K_3K_4[CN^-]^4\right)}$ = 4.79 10$^{-3}$ M**
**$s$ = 2.40 10$^{-3}$ M**

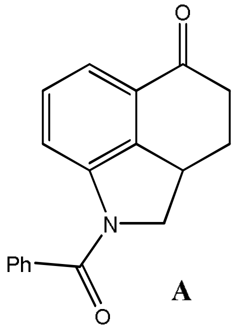
**6.4** **[OH$^-$] = $\sqrt[3]{2\cdot K_{ps}\cdot\left(1 + K_1K_2K_3K_4[CN^-]^4\right)}$ = 4.47 10$^{-3}$ M**
**$s$ = 2.24 10$^{-3}$ M**
**err % = [(2.24-2.40) / 2.40]·100 = 6.7 %**

**6.5** **83 µg / (207.2 g mol$^{-1}$ · 0.10 L) = 4.0 µM**

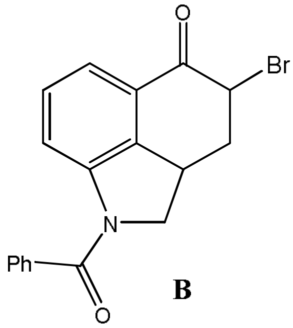
**Considerando il seguente equilibrio:**
**$[Ca(EDTA)_2]^{2-} + Pb^{2+}$ => $[Pb(EDTA)_2]^{2-} + Ca^{2+}$**
**la costante è $K' = K_{(Pb)} / K_{(Ca)}$**
**dato che c'è una forte complessazione e un eccesso di ioni calcio rispetto all'EDTA, l'EDTA è completamente legato o al Ca o al Pb.**
**Dato che $[Pb(EDTA)_2]^{2-}$ << $[Ca(EDTA)_2]^{2-}$ la concentrazione reale di $Ca^{2+}$ e $Ca(EDTA)_2^{2-}$ è praticamente identica a quella iniziale nella soluzione modello. Quindi:**
**$[Pb(EDTA)_2^{2-}] / [Pb^{2+}] = K'\,[Ca(EDTA)_2^{2-}] / [Ca^{2+}]$ = 8.0 10$^6$**

**6.6** **0.4 = $e^{-k\cdot 2}$ → k = 0.458 h$^{-1}$**
**$t_{1/2}$ = ln 2 / 0.458 h$^{-1}$ = 1.5 h**

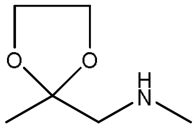
**7.1**



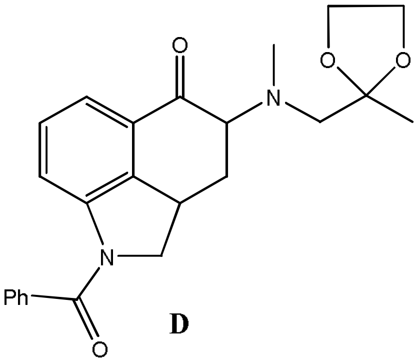
**A**



**B**



**C**



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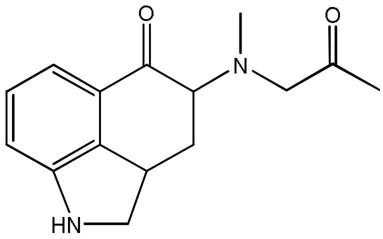
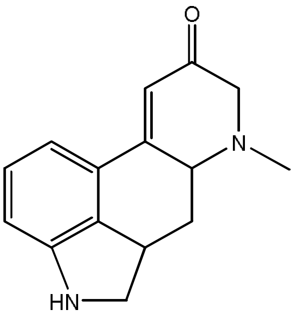
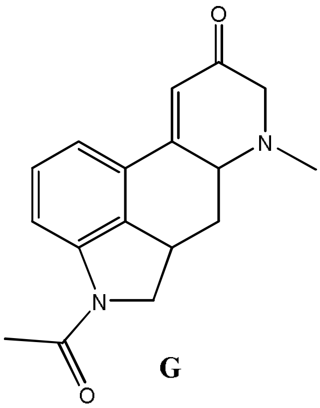


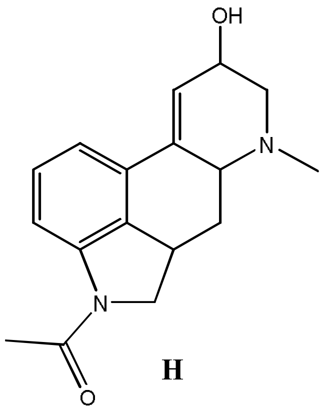
**E**



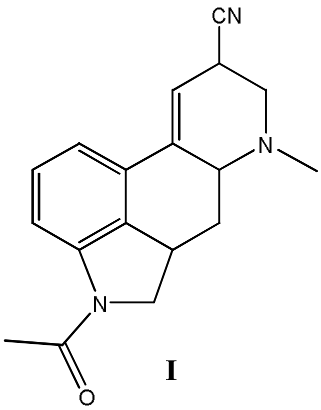
**F**



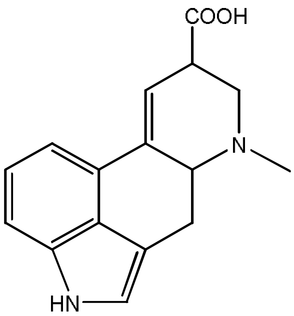
**G**



**H**

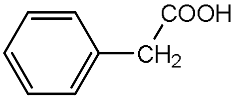


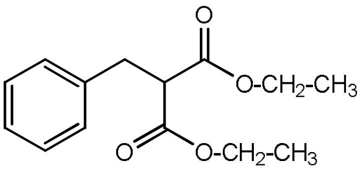
**I**



**Acido Lisergico**

**7.2** **Acido lisergico + $PCl_5/POCl_3$ poi $NHEt_2$ → LSD-25** (CA, 57, 5979 (*1962*).)
**oppure**
**Acido lisergico + SO3-DMF poi $NHEt_2$ → LSD-25** **(**JOC, 24, 368 (*1959*).)

**8.1** 


**8.2** 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