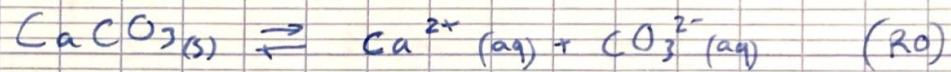


IE: CHEMISTRY * 1

Exercise n° 1:



1) $k_s = \frac{[\text{Ca}^{2+}] \cdot [\text{CO}_3^{2-}]}{[\text{CaCO}_3]} \quad (\text{R1})$

0,8

2) $\Delta_r G^\circ_{298} = \Delta_r H_{298} - T \Delta_r S^\circ_{298}$

$$\begin{aligned}\Delta_r H_{298} &= \Delta_f H(\text{Ca}^{2+}) + \Delta_f H(\text{CO}_3^{2-}) - \Delta_f H(\text{CaCO}_3) \\ &= -542,8 - 677,1 + 1207,1\end{aligned}$$

$$\Delta_r H_{298} = -12,8 \text{ kJ.mol}^{-1}$$

$$\begin{aligned}\Delta_r S_{298} &= \Delta_f S(\text{Ca}^{2+}) + \Delta_f S(\text{CO}_3^{2-}) - \Delta_f S(\text{CaCO}_3) \\ &= -53,1 - 56,9 - 88,7 \\ &= -198,7 \text{ J.mol}^{-1}.K^{-1}\end{aligned}$$

$$\Delta_r G^\circ_{298} = -12800 + 198,7 \times 298$$

$$\Delta_r G^\circ_{298} = 46412,6 \text{ J.mol}^{-1}$$

3) at equilibrium we have $0 = \Delta_r G^\circ + RT \ln(k_s)$

0,75

$$\text{hence } k_s = \exp\left(-\frac{\Delta_r G^\circ_{298}}{RT}\right) = 7,317 \times 10^{-9}$$

$$pK_s = -\log(k_s) = 8,136$$

1

4) $8,136 \approx 8,35$

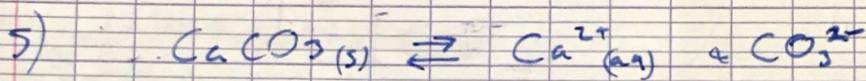
We get $\frac{|8,35 - 8,136|}{8,35} = 0,0256$

Q25

through the calculations it seem that we made an error of 2,56%.

- we conclude that our result is coherent.

$pK_s = 8,35$



IS:	n_0	s	0
EQ	$n_0 - s$	s	s

$K_s = s \times s$ hence $s = \sqrt{K_s} = \sqrt{10^{-8,35}}$

Q75

$s = 6,683 \times 10^{-5}$ mol.

(that can be dissolved in 1L)

6) when $\text{CO}_2(aq)$ is dissolved in the ocean it creates H_3O^+ ions, and they indicate the pH:

$\text{as } \text{pH} = -\log [\text{H}_3\text{O}^+]$ and (\log is an increasing function)

\Rightarrow the pH decreases as $[\text{H}_3\text{O}^+]$ increases.

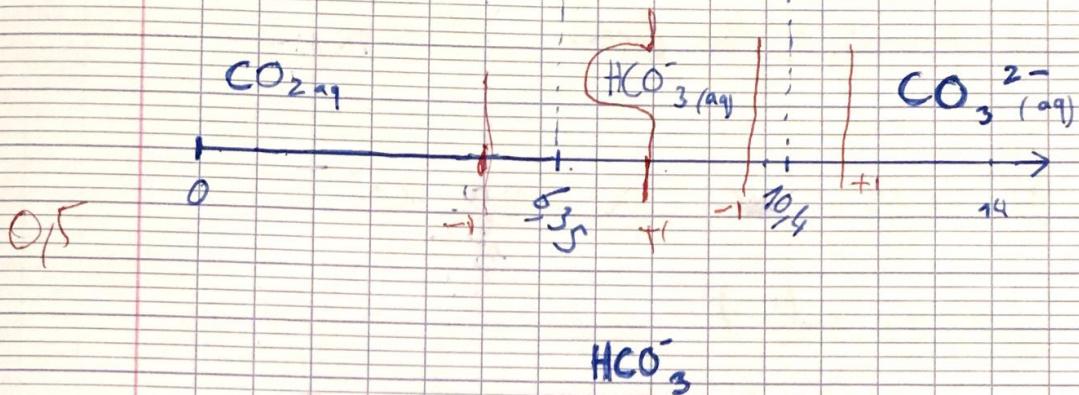
7) $K_{x1} = \frac{[\text{HCO}_3^-]/c_0 \times [\text{H}_3\text{O}^+]/c_0}{[\text{CO}_2]/c_0}$ eq

Q75

$K_{x2} = \frac{[\text{CO}_3^{2-}] \times [\text{H}_3\text{O}^+]/c_0}{[\text{HCO}_3^-]/c_0}$ eq

? 8) we know that: $pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \Rightarrow ?$

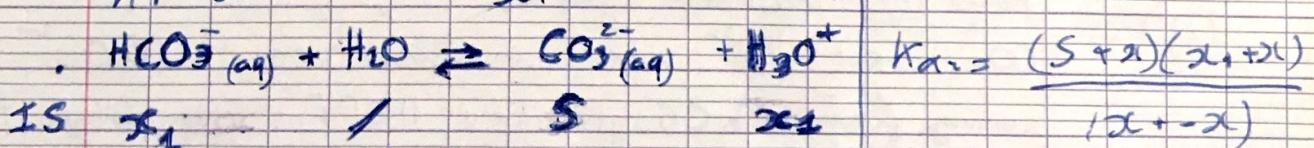
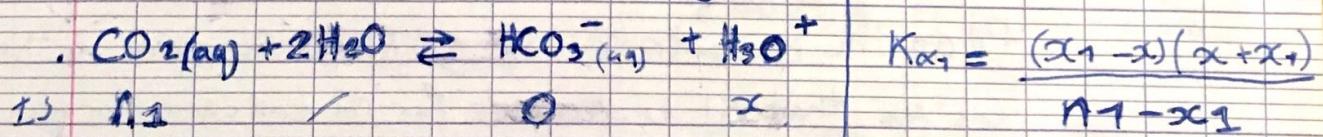
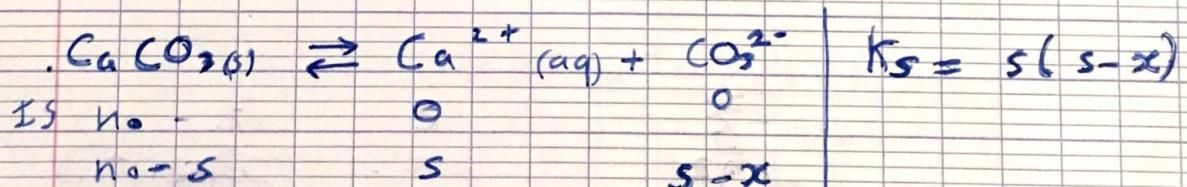
\downarrow
we need to
global solution
 \downarrow
 pK_a



$$9) s = [Ca^{2+}] = [CO_2(aq)] + [HCO_3^-] + [CO_3^{2-}] \quad \lambda^2 = K_s$$

$$K_s = [Ca^{2+}] \times ([CO_2(aq)] + [HCO_3^-] + [CO_3^{2-}])$$

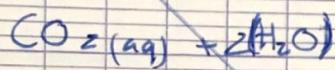
$$K_s = [Ca^{2+}] \times \left(\frac{[HCO_3^-] \times [H_3O^+]}{K_{a_1}} + \frac{[CO_3^{2-}] \times [H_3O^+]}{K_{a_2}} + [CO_3^{2-}] \right)$$



Q 25

10) When dissolved in the ocean CO_2 is in liquid form and dissolves into HCO_3^- as it is, at $\text{pH} = 8$ predominant in this form.

9) equilibrium of CO_2 and $\text{HCO}_3^{\text{-}}$.



13) As the concentration of $\text{CO}_2(\text{aq})$ increases in the ocean we see that it is easier for the calcareous organisms to dissolve hence they disappear faster.

Q 25

CO_2 creates H_3O^+ which in turn turns the CO_3^{2-} coming from CaCO_3 into HCO_3^- . This obliges the CaCO_3 to dissolve even more to reach their levels.

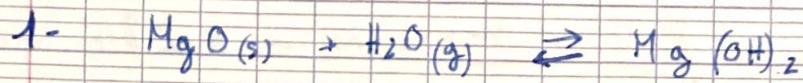
Conclu: CO_2 dissolves CaCO_3 .

4

Pierre
Retelle

Exercise n°2

Q25



$$2 - V = N - r - r' + n - \varphi$$

Q78

$$V = 3 - 1 - 0 + 2 - 3 = 1$$

this chemical reaction only has one degree of liberty, hence we only have to set 1 variable as $P = T$ and we can totally define the system.

$$3 - \Delta V = 0 \quad V = 10.0 \text{ L} \quad T = 150^\circ\text{C} \rightarrow 423 \text{ K}$$

since the water is being added at a temperature $T > 100^\circ\text{C}$ which is the ebullition temperature of water at $P_E = 1 \text{ bar}$ and that the equilibrium is reached when the system has a pressure of 1 bar, the water can only be gas.
Moreover 1 bar $\approx 10^5 \text{ Pa}$ which is the pressure after which water becomes liquid $\rightarrow 15^\circ\text{C}$?

4) If we introduce $n = 0.222$ mole of water

$$\text{we will have } P_E = \frac{nRT}{V} = \frac{0.222 \times 8.314 \times 423}{10 \times 10^{-3}} = 78073.4 \text{ Pa} = 0.78 \text{ bar}$$

since $0.78 < P_E = 1 \text{ bar}$
the system can't reach an equilibrium because the water pressure must be at 1 bar for any excess water added to react.

5) the minimum number of n would be

$$n_{\min} = \frac{P_{eq} V}{R T} = \frac{100000 \times 0,02}{8374 + 423} \approx 0,284 \text{ mol}$$

0775

we round up to be sur
 $n_{\min} \approx 0,285 \text{ mol}$

6) n_{\max} is the number of moles that consume all the $\text{MgO}_{(s)}$
 while keeping the water pressure at 1 bar:

$$n_{\max} = n_{\min} + \frac{m(\text{MgO})}{M(\text{MgO})}$$

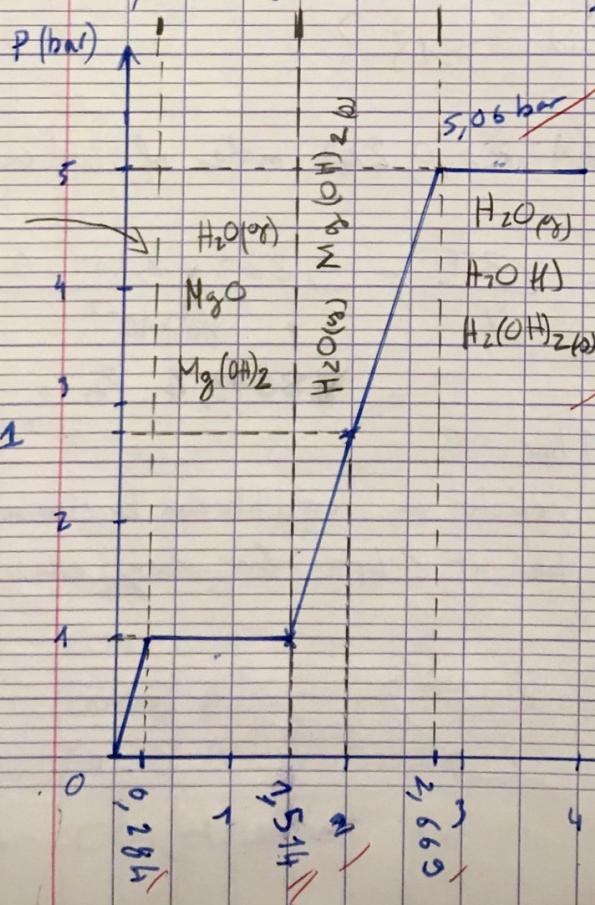
$$n_{\max} = \frac{P_{eq} V}{R T} + \frac{m(\text{MgO})}{24,3 + 16} = 1,514 \text{ mol}$$

$$M = \frac{m}{n}$$

$$n(\text{MgO}) = 1,230 \text{ mol}$$

7) a) $P = f(n)$

$$P_{n=2} = \frac{(n-1,23) RT}{V} = 2,71 \text{ bar}$$



b) ✓

c) ✓

8) a) $n = 1,00 \text{ mol}$ of water added

$$\cdot n(H_2O_{\text{aq}}) = 0,284 \text{ mol}$$

$$0,75 \cdot n(MgO) = \frac{m_i(MgO)}{M} - (n - n_{\min}) = 0,514 \text{ mol}$$

$$\cdot n(Mg(OH)_2) = (n - n_{\min}) = 0,716 \text{ mol}$$

b) $n = 2,00$ added

$$\cdot n(H_2O_{\text{aq}}) = n - \frac{m_i(MgO)}{M} = 0,770 \text{ mol.}$$

$$\cdot n(MgO) = 0 \text{ mol}$$

$$0,5 \cdot n(Mg(OH)_2) = \frac{m_i(MgO)}{M} = 1,23$$

$$9) \cdot n_{\min} = \frac{P_s V}{R T} + n_i(MgO) = 2,669 \text{ mol.}$$

10) ✓