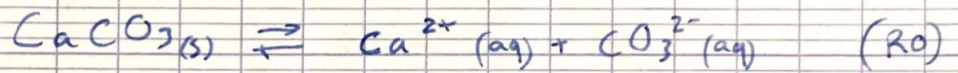


Exercise n° 1:



0,5

$$1) K_s = \left( \frac{[\text{Ca}^{2+}]}{c_0} \cdot \frac{[\text{CO}_3^{2-}]}{c_0} \right)_{\text{eq}}$$

$$2) \Delta_r G_{298}^\circ = \Delta_r H_{298}^\circ - T \Delta_r S_{298}^\circ$$

$$\begin{aligned} \Delta_r H_{298}^\circ &= \Delta_f H(\text{Ca}^{2+}) + \Delta_f H(\text{CO}_3^{2-}) - \Delta_f H(\text{CaCO}_3) \\ &= -542,8 - 677,1 + 1207,1 \\ \Delta_r H_{298}^\circ &= -12,8 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

1,75

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

$$\begin{aligned} \Delta_r G_{298}^\circ &= -12800 + 198,7 \times 298 \\ \Delta_r G_{298}^\circ &= 46412,6 \text{ J} \cdot \text{mol}^{-1} \end{aligned}$$

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

0,75

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

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

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

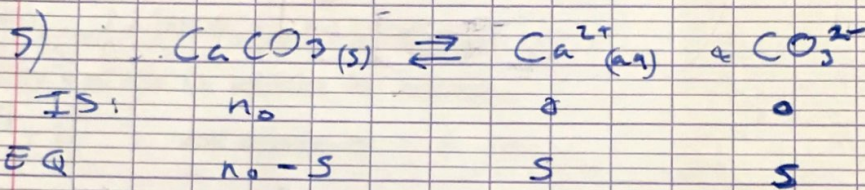
we get  $\frac{|8,35 - 8,136|}{8,35} = 0,0256$

0,25

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

- we conclude that our result is coherent.

$pK_s = 8,35$



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

0,75

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

(that can be dissolved in 1L)

6) when  $CO_2(aq)$  is dissolved in the ocean it creates  $H_3O^+$  ions, and they indicate the pH:

0,25

as  $pH = -\log [H_3O^+]$  and (log is an increasing function)

$\Rightarrow$  the pH decreases as  $[H_3O^+]$  increases.

7)  $K_{\alpha 1} = \frac{[HCO_3^-]/c_0 \times [H_3O^+]/c_0}{[CO_2]/c_0}$  Eq

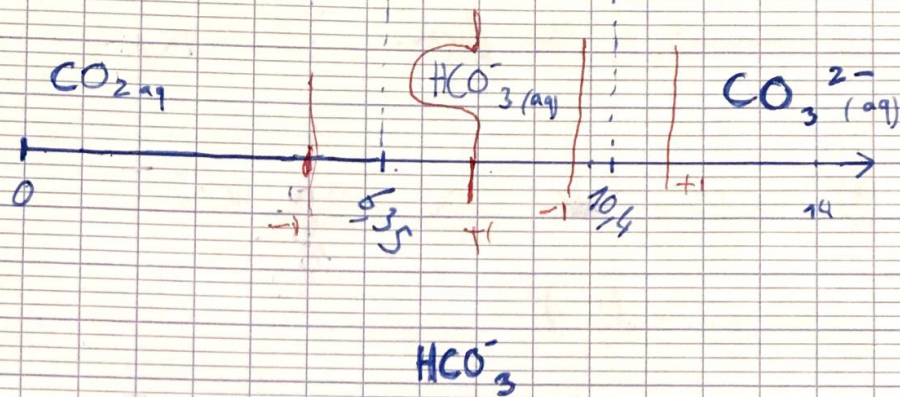
0,15

$K_{\alpha 2} = \frac{[CO_3^{2-}]/c_0 \times [H_3O^+]/c_0}{[HCO_3^-]/c_0}$  Eq

7 8) we know that:  $pH = pKa + \log\left(\frac{[B]}{[A]}\right) \rightarrow ?$

← we need to global solution pKa.

0.5



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

0.5

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

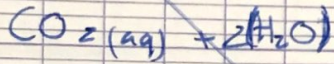
$$K_s = [Ca^{2+}] \times \left( \frac{[HCO_3^-] \times [H_2O^+]}{K_{a1}} + \frac{[CO_3^{2-}] \times [H_3O^+]}{K_{a2}} + [CO_3^{2-}] \right)$$

	$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}$	$K_s = s(s-x)$
IS	$n_0$	0
	$n_0 - s$	s
		$s - x$
	$CO_2(aq) + 2H_2O \rightleftharpoons HCO_3^-(aq) + H_3O^+$	$K_{a1} = \frac{(x_1 - x)(x + x_1)}{n_1 - x_1}$
IS	$n_1$	0
	$n_1 - x_1$	$x_1 - x$
		$x + x_1$
	$HCO_3^-(aq) + H_2O \rightleftharpoons CO_3^{2-}(aq) + H_3O^+$	$K_{a2} = \frac{(s+x)(x_1+x)}{(x_1-x)}$
IS	$x_1$	s
	$x_1 - x$	$s+x$
		$x_1+x$

0,25

10) when dissolved in the ocean  $\text{CO}_2$  is in liquid form and dissolves into  $\text{HCO}_3^-$  as it is, at  $\text{pH} = 8$  predominant in this form.

9) equilibrium of  $\text{CO}_2$  and  $\text{HCO}_3^-$ .



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.

$\text{CO}_2$  react  $\text{H}_2\text{O}^{+}$  which in turn turns the  $\text{CO}_3^{2-}$  coming from  $\text{CaCO}_3(\text{s})$  into  $\text{HCO}_3^-$ . This obliges the  $\text{CaCO}_3$  to dissolve even more to reach their  $K_s$ .

0,15

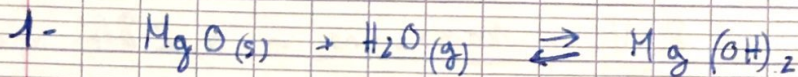
Concl:  $\text{CO}_2$  dissolves  $\text{CaCO}_3$ .

4

Pierre  
Retelle

## Exercise n°2

Q25



Q75

$$2- V = N - r - r' + n - P$$
$$V = 3 - 1 - 0 + 2 - 3 = 1$$

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

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

not done!  
since ~~the~~ water is being added at a temperature  $\theta > 100^\circ\text{C}$  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.  
More over 1 bar  $\rightarrow 1.506 \text{ bar}$  which is the pressure after which water becomes liquide  $\rightarrow 15^\circ$ ?

4- If we introduce  $n = 0,222$  moles of water

$$\text{we will have } P = \frac{nRT}{V} = \frac{0,222 \times 8,314 \times 423}{10 \times 10^{-3}}$$
$$= 78073,4 \text{ Pa} = 0,78 \text{ bar}$$

1  
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

$$n_{\min} = \frac{P_{\text{eq}} V}{RT} = \frac{105000 \times 0,02}{8,314 \times 423} = 0,284 \text{ mol}$$

0,75

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

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

0,75

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

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

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

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

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

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

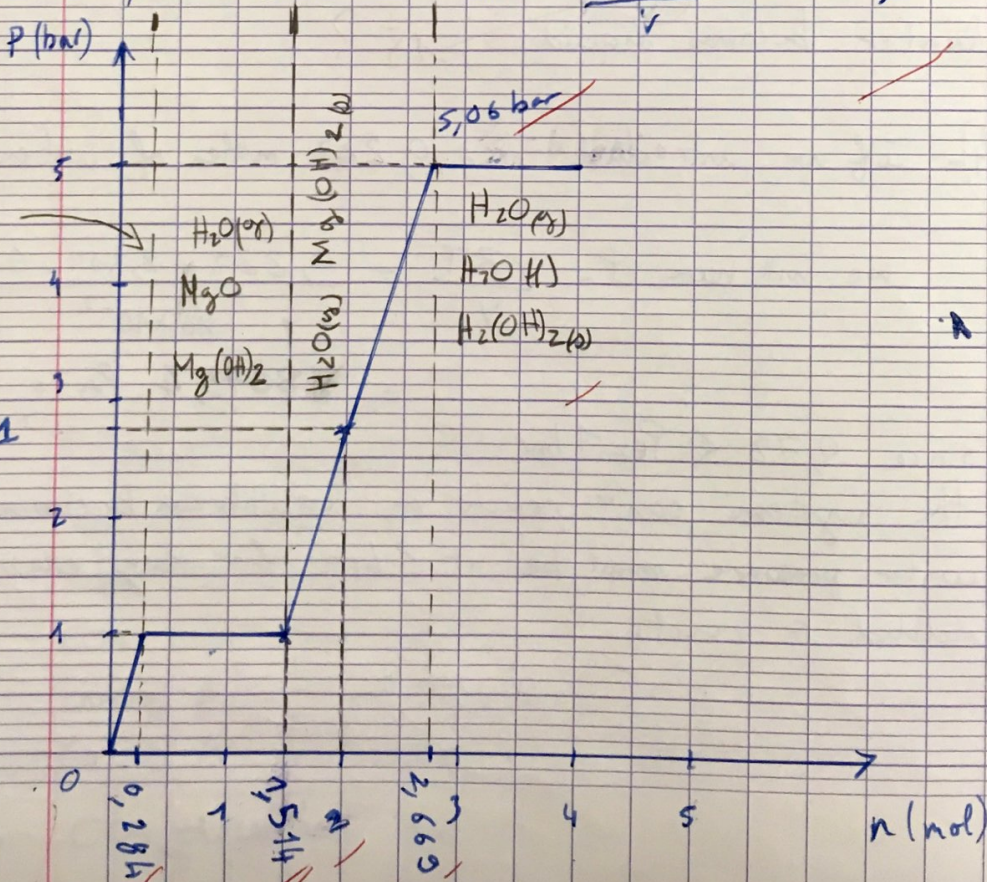
0,75  
 $\text{H}_2\text{O(g)}$   
 $+ \text{MgO(s)}$

0,75  
 2,71

0,75

1

0,75



b) ✓

c) ✓

8) a)  $n = 1,00$  mol of water added

$$n(\text{H}_2\text{O}_g) = 0,284 \text{ mol}$$

0,75

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

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

b)  $n = 2,00$  added

$$n(\text{H}_2\text{O}_g) = n - \frac{m_i(\text{MgO})}{M} = 0,770 \text{ mol.}$$

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

0,5

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

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

1

10) ✓