CERAMIC AND COLLOIDAL PROCESSING - EXERCISES

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Exercises 3

1. What mineral powders (and their percentages) are used for the production of hard porcelain,

The composition is 25% Quartz, 50% Kaolin (clay), 25% Feldspar

2. (a)What are the simple models describing the decomposition of a salt or the oxidation of a metal for the synthesis of a ceramic powder? (b)What are the steps that can limit the kinetics of fluid-solid reactions?

a) There are two models which describe the kinetics of solid-fluid reactions (thus which apply to the decomposition of a salt or the oxidation of a metal):
   i) the gradual conversion model
   ii) the shrinking core model

b) i) mass transfer of the reactive or product fluid through a surface film (the boundary layer)
   ii) diffusion of the gaseous and / or product reactant through the solid product layer towards the interface of the unreacted core
   iii) chemical reaction or decomposition at the surface (interface) of the shrinking reactant core

3. Zinc blende particles having a radius R = 1 mm are calcined in a gas flow of 8% oxygen at 900 ° C and 1 atmosphere. The stoichiometry of the reaction is:

2. $ZnS + 3\ O_2 \longrightarrow 2\ ZnO + 2\ SO_2$

Assuming the reaction progresses according to the shrinking core model
(a) Calculate the time required for complete conversion of a particle and the relative resistance due to diffusion through the product layer during this operation.
(b) Do the same calculation for particles with radius R = 0.05 mm.

Problem data:
Density of solid $\rho_B = 4.13\ g / cm^3 = 0.0425\ Mol / cm^3$
Reaction rate constant $k_s = 2\ cm / sec$.
Ideal gas constant $R_g = 82.057\ atm.cm^3 / K\ .\ Mol$
For gases in the ZnO layer, $D_p = 0.08\ cm^2 / sec$, $b = 2/3$

Note that the resistance of the laminar gas layer can be safely neglected as long as the growth of the product layer is taking place, also considering only the effects of mass transfer and $C_a = P_{O2} / R_g.T$ (Mol / cm^3)).

2 ZnS + 3O_2 → 2 ZnO + 2SO_2 – rearrange so that the reactive gas has a stoichiometric coefficient of 1

2/3ZnS + O_2 → 2/3 ZnO + 2/3SO_2

Particles of zinc blend

T= 900° = 1173 K p= 1 atm, 8% O_2

The time that is required for the total conversion: $T_T = T_F + T_D + T_R$

We neglect T_F

a) For R=1mm=0.1cm

$$T_D = \frac{\rho_B \cdot R^2}{6b \cdot Dp \cdot Ca}$$

$$Ca = \frac{Po_2}{Rg \cdot T} = \frac{0.08}{82.057 \cdot 1173} = 8.31 \cdot 10^{-7} \text{ mol/cm}^3$$

$$\Rightarrow T_d = \frac{0.0425 \cdot (0.1)^2}{6 \cdot \frac{2}{3} \cdot 0.08 \cdot 8.31 \cdot 10^{-7}} = 1597.95s$$

$$T_R = \frac{\rho_B \cdot R}{b \cdot kg \cdot Ca} = \frac{0.0425 \cdot 0.1}{\frac{2}{3} \cdot 2 \cdot 8.31 \cdot 10^{-7}} = 3835.74s$$

$$\Rightarrow T_T = 5433.7s$$

Relative resistance due to diffusion through the product layer: $100\frac{T_D}{T_T} = 29.41\%$

b) for R=0.005 cm

$$T_D = \frac{0.0425 \cdot (0.005)^2}{6 \cdot \frac{2}{3} \cdot 0.08 \cdot 8.31 \cdot 10^{-7}} = 4s$$

$$T_R = \frac{0.0425 \cdot 0.005}{\frac{2}{3} \cdot 2 \cdot 8.31 \cdot 10^{-7}} = 191.8s$$

$$\Rightarrow T_T = 195.8s$$

And therefore… $\frac{T_D}{T_T} \cdot 100 = 2.04\%$

What are the consequences of the size reduction on the reaction kinetics?

We see that when the radius decreases, the reaction takes place more quickly. But diffusion is less important as a resistance. The rate limiting step becomes chemical reaction and even TF can be reconsidered.

4. Give a typical solid-solid reaction to produce a ceramic powder.

$SiO_2(s) + 3C(s) \rightarrow SiC(s) + 2CO(g)$

However other intermediate reactions can occur → volatilization of an intermediate product

a) $SiO_2 + C \rightarrow SiO + CO$
$2SiO_2 + SiC \rightarrow 3SiO(g) + CO(g)$
$SiO_2 + Si \rightarrow 2\ SiO$

b) $SiO + 2C \rightarrow SiC + CO$
$SiO + 2SiC \rightarrow 2Si + CO$

The dominant forward reaction will depend on the thermodynamics of each individual reaction.

5. How does the decomposition temperatures of $CaCO_3$, $BaCO_3$ and $MgCO_3$ vary as a function of the partial pressure of CO_2 in the gas of a furnace i) standard state (1 atm of CO_2) ii) ambient air (pCO_2 $5x10^{-4}$ atm) iii) nitrogen with 10ppm CO^2 (10^{-5} atm)

$CaCO_3$ T= decomposition temperature

i)	$P_{CO2} = 1$ atm	T = 1160 K
ii)	$P_{CO2} = 5 \cdot 10^{-4}$ atm	T = 825 K
iii)	$P_{CO2} = 10^{-5}$ atm	T = 710 K

$BaCO_3$

i)	T =1110K
ii)	T = 820 K
iii)	T = 710

$MgCO_3$

i)	675 K
ii)	500 K
iii)	450 K

We see that the temperature drops with the decrease in the partial pressure of CO2 which is a function of its partial pressure. Gas pressure P↓ T reaction ↓