The references
1. Elements of Ceramics  By Norton F.H
2. Introduction to Ceramic  By Kirgory
3. Characterization of Ceramics  By Warrall
4. Ceramic Drying  By R.W. Ford
5. Properties of Ceramics Raw Materials  By Warrall
6. Refractories  By Norton F.H
Ceramics - Product manufactured by heat treatment of a material or mixture of materials which is inorganic and non-metallic.

Ceramic products:
- Table-ware (saucers, cups, plates, etc.)
- Bricks
- Tiles
- Earthenware
- Porcelain
- Acid resisting ware for chemical plants.

Product used in Refractories

Classification of Ceramics

- Products used at elevated temperature
- Products used at or slightly above room temperature

- Porous body
- Vitreous body

- Porous body
- Nitreous body
Porous body & refractories such as Al₂O₃, SiO₂
البياضات الخفيفة والصلبة مثل السكرین وصلبة الزز/documentation

Fire clay ware
سگانیت للحزمة

Insulating refractories
حلاطین للحزمة

Vitreous body & opal refractories often made from pure single materials
كمال مادة للحزمة

Porous body: Like, Heavy clay, Bricks, Tiles, Bowls, Conduits, Pipes, sanitary fire clay, pottery
كمال مادة للحزمة

Vitreous body: Fire clay, porcelain, Electrical porcelain, chemical stone
كمال مادة للحزمة

appearance and color, not attention is given mechanical properties, Electrical properties, Resistance to chemical & Resistance to temperature.
كمال مادة للحزمة

* Cement and Glasses *
كمال مادة للحزمة

* inorganic, non-metallic * has been developed for Electrical, nuclear power, and for Engineering industries.
Ex. Rutile: TiO₂ ⇒ used for making ferro-electric materials

Talc: Electrical insulator

Alumina, Zirconia, Thoria ⇒ for refractories and as electric insulators.

The major process of making ceramic material:

1. Raw materials
2. Purification
3. Size Adjicement
4. Mix materials mixing in required proportions
5. Product shaped
6. Dried
7. Fired

Row material of Ceramic

1. Clay
2. Silica
3. Flux (Feldspar)
4. Other
Firing: material added to the clay to enable it to fuse more readily, it also lower the temperature at which liquid forms during firing, this liquid when cooled it forms aglass which bound the grains of the clay to gather.

Alkalies: \( \text{K}_2\text{O}, \text{Li}_2\text{O}, \text{Na}_2\text{O}, \text{Al}_2\text{O} \)

Lime: \( \text{CaO}, \text{MgO} \)

Clay: Mineral or aggregate of minerals, clay is responsible of the ceramic characteristics.

Quartz, mica, FeO

Two major groups of clay:

- Kaolinite group: \( \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \)
  1. Kaolinite
  2. nacrite
  3. dickite
  4. halloysite

- Montmorillonite group: \( \text{Al}_2\cdot \text{Si}_4\text{O}_10(\text{OH})_2 \)
  1. Montmorillonite
  2. Montmorillonite
  3. Beidellite
  4. Hectorite

Chlorite, illite, Bentonite.
Granite

Formation of clay

\[ \text{Igneous Rx.} \]

\[ \begin{align*} 
\text{Granite:} & \quad \text{Mica: } K_2O \quad 3Al_2O_3 \quad 6SiO_2 \quad 2H_2O \\
\text{Quartz:} & \quad SiO_2 \\
\text{Feldspar:} & \quad K_2O \quad Al_2O_3 \quad 6SiO_2 \\
\text{Hydrous Aluminum Silicate:} & \end{align*} \]

\[ K_2O \quad Al_2O_3 \quad 6SiO_2 + H_2O \rightarrow Al_2O_3 \quad 2SiO_2 \quad 2H_2O \\
- \quad K_2O \\
- \quad 4SiO_2 \\
\rightarrow \text{Kaolinite} \]

Hexagonal

Origin of Clay

1. Residual clay (primary clay):
   Clay formed from granite and deposited at its place of origin.

2. Sedimentary clay (secondary clay):
   Clay formed from Ig. Rx and transported by wind or rain or rivers to another place far away from place of origin and then redeposited.
Structure of Kaolin

Gibbsite Layer Al(OH)₃
Silica Layer SiO₄

Silica Layer

Gibbsite Layer Al₂O₃
The stacking of layers on one another to form a crystal will give the difference between the minerals of kaolinite group. The direct stacking means nacrite, and any displacement in the stacking means the other types of minerals in this group.
The structure of Montmorillonites

1. Pyrophyllite
2. Talc (steatite) parent minerals of Mont. group

Silica

Gibbsite

Silica

Pyrophyllite

Other minerals of this group formed by replacement of Al to the silica in the tetrahedral layer and the replacement of Al in the octahedral layer by Mg or Fe

مياط الماء مختله احمد شام اصبعلا الالح 7 مي مي مي مي

Fe or Mg or Al, Al, Al, Al, Al
Plasticity: If a material can change its shape without cracking or breaking, then the material is called plastic material.

If a body of high clay content, i.e., has a high plasticity property, which allows the material to be deformed (or shaped) without cracking or breaking, under the influence of an applied force, and to retain its new shape when the deforming force is removed.

Also, plasticity depends on the water content.

The finer the material, the greater the plasticity.

The higher the proportion of clay in the material of Ceramic and its more plastic type of clay, the more water is required to produce workable consistency.
* Good plasticity the lower the moisture content at which the body can be worked the better, since the high moisture content leads to high shrinkage in drying, which may cause cracking and breaking.

Ideally the body should be developed high plasticity at low moisture content; this would make for easy shaping and safe drying; this combination does not occur in practice; however, the compromise must be made between having enough water present to develop the plasticity required for shaping and the same time keeping the moisture content low enough to make drying safe.

The particles of the clay are platy in shape, and many of the atoms making up the grains of the clay joined the other atoms only on one side. To satisfy the unbalance the surface atom attract water molecules to the surface of the clay grains this water layer lubricate the movement of one clay plat over one another to form plasticity.
Atterberg method to measure plasticity:

Simplest method of determining the plastic limit (the liquid limit (LL) minus the plastic limit (PL) by subtraction)

Plasticity Index (PI) calculator

Physical properties of clay minerals

- Particle size and shape
- Kaolinite group: 0.1 - 2 μm, sometimes 20 μm
- Montmorillonites: 0.01 - 2 μm
- Hexagonal system: partial system platting in shape

- Particles are hard and cannot be broken down easily
- The smallest the particles the highest plasticity

- $G$ (Specific Gravity) = 2.6

Heating the raw material (clay):
Kaolinite, Naenite, dickite

\[
\text{Al}_2 \text{Si}_2 \text{O}_5 \cdot \text{(OH)}_4 \xrightarrow{450^\circ \text{C}} \text{Al}_2 \text{Si}_2 \text{O}_7 + \text{H}_2 \text{O}
\]

meta-kaolinite

The structure still not change as whole but on increasing temperature to 900 - 1000°C
if decomposed to \( \text{Al}_2 \text{O}_3 \) & \( \text{SiO}_2 \)

\[
\text{Al}_2 \text{O}_3 ( \text{c} \text{Al}_2 \text{O}_3 )
\]

\[
3 \text{Al}_2 \text{Si}_2 \text{O}_7 \xrightarrow{1000^\circ \text{C}} 2 \text{Al}_6 \text{Si}_2 \text{O}_{13} + 4 \text{SiO}_2
\]

dickite

silica

100°C: every moisture and hygroscopic water driven off

950 - 500°C: Hydroxyle group driven off (dehydroxylation)

400 - 700°C: Organic materials burn off

300 - 700°C: vitrification (glass formation)

start at above 900°C
Montmorillonite

100 – 200 °C. The water adsorbed between silica layer is evolved. The silica layers become closer together and the clay mineral break down and all water removed. At about 1200 °C. Mullite, Cristabolite + Cordierite, and spirel are formed.

All clays on heating fuse to viscous liquid (silica + impurities (Na2O, H2O, CaO, MgO)) lower the melting point of the silica enabling liquid to form at lower temperature 1200 °C. For this reason they called flux oxides.

On Cooling the liquid that was produced does not crystallized completely, but mostly solidifies to form glass. During firing the liquid that forms when the clay begins to fuse fill up the pores spaces in the clay Consequently the volume decrease i.e. the shrinkage occurs. Also porosity decreases this process called Vitrification.
Effect of impurities on clay

1. % of occurrence
2. Grain size of clay
3. Nature of the substance
4. Physical conditions: temp., heating, furnace type

Impurities (Na₂O, K₂O, CaO, MgO)

These oxides ions fill in the holes in the Si-O net work.

Material and Oxides occur in clay of ceramic.
It is added to clay to supply at least a portion of the glassy phase during firing, which is needed for strength and translucency.

- reduce dry strength
- reduce drying shrinkage
- form glass matrix.
- Reduce refractoriness

Silica

Crystalline, quartz, sandgrains, chalcedony
quantzite, chert, flint

Non-crystalline (amorphous), Opal

- 1. Reduces drying shrinkage
- 2. Reduces plasticity
- 3. Allow the escape of gases during firing
- 4. During firing it combines with basic oxides to form glass which is responsible for the strength.

Although quartz and sandgrains is used, but flint is the most recommended.
Three main Crystalline forms of silica

i. Quartz (MP) \( \frac{4}{3} \) Si O \(_3\) diffuse in arrangement
ii. Tridymite \( \frac{1}{3} \) Si O \(_3\) of O around (Si) atom
iii. Cristobalite (MP) \( \frac{1}{3} \) Si

(ii), (iii) are high temperature form of silica, melting point 1710 C°

(i) stable up to 870 C°

- The change from quartz to Tridymite & Cristobalite involve breaking Valency bonds ...(Conversion)

- Inversion is the change of the three forms of silica as a structural change, it involve the rotation of Valency bonds between Si & O atoms.

Carbonate

Dolomite Ca Mg (CO\(_3\))\(_2\)
Calite Ca CO\(_3\)
Aragonite Ca CO\(_3\)
Chromite Cr\(_2\) Fe CO\(_3\)

It is used when low silica materials is desired.

Iron Oxides

Fe\(_2\)O, Fe\(_3\)O, FeS

It is used mostly for the colour it gives to the Ceramic material. It may reduce refractiness
Methods used for the identification and characterization of Clays:

1. Chemical analysis, X-ray fluorescence
2. X-Ray Diffraction
3. Differential Thermal Analysis
4. Infrared absorption spectrometry
5. Optical Microscopy
6. Electronic Microscopy
DTA: It depends on the detection of the heat given off or absorbed when phase change occurs. The apparatus contains two compartments one for the sample and the other for an inert sample which does not undergo the change to be measured. Each compartment is provided with a thermocouple for measuring the temperature (T) of the sample material.
and also the difference in temperature between the inert and the specimen ($\Delta T$) to achieve uniformity of temperature the specimen holders is placed inside acylindrical refractory block which fits inside electrically heated tube furnace.

On raising the temp. 100±6/min the thermo couple reading recorded automatically on a chart record.

![Diagram](image)

If no reaction occurs the temp of the inert material will be the same as the specimen but when the reaction in volume heat change, the temp of the specimen will deviate from that of the inert material according to whether.

The reaction is exothermic or endothermic if $\Delta T$ plotted on $T$ peak will show in every phase change the zero line called base line.
Inversion and Conversion

The main form of silica is二氧化硅:

- Quartz
- Tridymite
- Cristobalite

Conversion: CO₂ → Stable up to 870°C
- Tridymite: Stability 870 - 1470°C
- Cristobalite: Above 1470 - 1710°C (melting point)

Fusion → Glass: i.e., non-crystallization
- CO₂ → 1470°C: Earthenware Cristobalite (1470 - 1870°C)

Tridymite

(Ca₂ or Fe₂) Catalyst: Considerable energy are evolved.

Inversion:

α Quartz $\xrightarrow{573°C}$ β Quartz

α Tridymite $\xrightarrow{1173°C}$ β₁ tridymite $\xrightarrow{1650°C}$ β₂ tridymite

α Cristobalite $\xrightarrow{220 - 280°C}$ β Cristobalite
Thermal expansion

material

\[ \alpha \rightarrow \beta \text{, tridyrite} \]

linear expansion

\[ 0.45 \]

\[ \alpha \text{ Cristabolite} \rightarrow \beta \text{ Cristabolite} 1\% \]

Can be used to prevent crazing cracking of glaze due to failure of tension.

Thermodynamics of reaction

Firing is the most important procedure of forming Ceramic. Firing is the most important procedure of forming Ceramic. Firing is the most important procedure of forming Ceramic.

Energy stable: stable phase; at any temp. level is the one having the lowest free energy.
Phase Rule: in general, the heat energy evolved is large (AH) in general, if the heat energy evolved is large (AH), the system has high stability. When two elements combined, those absorbed or evolve energy stability, the system is more stable. 

Heat of formation: it is the energy absorbed or evolved when one mole of a compound is formed from its elements in their standard states.

Phase: a physical homogeneous but mechanically separable portion of system which is physically homogeneous and is bounded by surface. It is usually composed of one substance.

Phases: stable or unstable, glass or high energy.
Components: are the smallest number of independent variables, constituents by means of which the composition of each phase can be qualitatively expressed.

Ex. Mg and O the components Mg, O
     MgO, O
     Mg, MgO

Equilibrium Diagram: It is a graphical representation of the phase rule as applied to a particular system.

Phase Diagram or Binary system

Clay heated to about 1500°C, reaction forms mullite + cristobalite

About 1595°C: liquid phase appears
1. Mullite melt at 1810°C.
2. Small additions of silica to alumina or alumina to silica results in reduction of the melts point.
3. The addition of 5% Al₂O₃ to silica reduce the Temp. from 1210°C the melting point of silica to ≈ 1600°C.
4. Further addition of Al₂O₃ cause an increase in melting point.
5. The composition of SiO₂ 95%, 5% Al₂O₃ is the composition of Cubic, i.e. the composition with minimum melting point.
6. At 72% Al₂O₃ : 38% SiO₂ we have the composition of Mullite 3Al₂O₃ : 2SiO₂ which has a melting point of 1850°C.

SiO₂  Al₂O₃
% 100  → SiO₂ decreases Al₂O₃ decrease

Phase diagram
7. All mixtures contain less than 72% Al₂O₃ will form liquid above 1595°. Compositions containing more than 72% Al₂O₃ first form liquid at 1850°C or higher temperature.

8. As Al₂O₃ content is increased from 72% the temperature at which liquid first forms increases until the melting point of Al₂O₃ is reached at a composition of 100% Al₂O₃.

Mining and Treatment of Raw Materials

Methods of Communication:

1. Simple Compression if it is brittle.
2. Impact Compression.
3. Impact too low in energy.
4. Striking one particle to another.
5. Abrasion causing sub division.
The changes which occur during firing the clay raw materials are:

1. Crystallization: \( \text{Al}_2 \text{O}_3 \) to form \( \text{Y} \)-crystalline and then to \( \alpha \)-crystals (Corundum) as the temperature increases from \( 500 \) to \( 1400 \) \( ^\circ \text{C} \).

2. Breaking down some of the crystals.

3. Evolution of some gases at high temperature due to the reactions either with \( \text{O}_2 \) or the decomposition of compounds:

\[
\begin{align*}
\text{CaCO}_3 & \rightarrow \text{CaO} + \text{CO}_2 \\
\text{MgCO}_3 & \rightarrow \text{MgO} + \text{CO}_2 \\
\text{CaSO}_4 & \rightarrow \text{CaO} + \text{SO}_3 \\
\text{C} + \text{O}_2 & \rightarrow \text{CO}_2 \\
\text{S} + \text{O}_2 & \rightarrow \text{SO}_2
\end{align*}
\]

These changes do not depend on the temperature only, but also on:

1. The maximum temperature, ii - The time required for the completion of the reaction, iii - Grain morphology i.e. size and shape, iv - The composition of the raw material.
Energy required to break down pieces of material is proportional to the new surface area produced i.e grain size.

\[ E = C_i \left( \frac{1}{D_2^2} - \frac{1}{D_1^2} \right) \]

- \( E \): energy spent per unit volume
- \( C_i \): Constant
- \( D_1 \): Initial grain size
- \( D_2 \): Final grain size

Kik (1885) \[ E = \log \left( \frac{D_1}{D_2} \right) \]

Diagram:
- Jaw crusher
- Cone crusher
- Roller crusher
- Toothed Roll
- Roll mill
- Hammer mill
1. Drying mixing:

For non-clay bodies, in non-clay bodies, binders and plasticizers or lubricating materials are added to dry mix. These materials serve to aid forming and shaping and size the body strength before firing. Material: organic materials e.g. wax, waxes ... etc., which burns after they do their function.

2. Plastic mixing:

In this type of mixing plasticity developed when water is added to the clay material or bodies containing clay materials so that we can get the required consistency. The addition of water to the clay is called Temporying. Then the whole material extruded into a plug machine, this pugging process is done under Vacuum why? 

3. Slip mixing:

Adding the clay mass is made at the large suspension is mainly used in pottery and fine ceramic. is known as slip. A suspension of powdered ceramic in liquid (water) is called slip.
**Forming Methods**

<table>
<thead>
<tr>
<th>Forming process</th>
<th>Pressure used</th>
<th>Physical state</th>
<th>Water content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slip casting</td>
<td>0</td>
<td>Fluid suspension</td>
<td>12 - 25%</td>
</tr>
<tr>
<td>Plastic forming</td>
<td>50 - 1000</td>
<td>Plastic mass</td>
<td>5 - 30%</td>
</tr>
<tr>
<td>Extrusion forming</td>
<td>1000 - 200000</td>
<td>Damp powder</td>
<td>5 - 10%</td>
</tr>
<tr>
<td>Dry pressing</td>
<td>3000 - 20000</td>
<td>Dry powder</td>
<td>0 - 2%</td>
</tr>
<tr>
<td>Isostatic pressing</td>
<td>5000 - 100000</td>
<td></td>
<td>0 - 15%</td>
</tr>
</tbody>
</table>

1. **Slip Casting**

   a/ Drain Casting:
   The slip is poured in the mold left for a short time and then drain out (by using porous plaster) as a mold, leaving a thin shell against the inside wall.

   b/ Solid Casting: the mold is filled with slip and left until casts into a solid piece.

High concentration of slip materials?
(2) Plastic forming

- The material, shape, and size of the pores and its porosity influence the mechanical properties of the final product.

- Organic plasticizers

- Differentiation shrinkage or cracking

(3) Dry pressing and semi-dry pressing

- Accuracy in size. No drying is required.
- Use with some types of bricks.

(4) Industrial porcelain product

- Dry pressing. In this case, the liquid and the water are dissolved and transformed into a solid.

- Insulators and capacitors.
1. The quality of products affected by:

   a. Rate of pressure rise
   b. Increasing pressure
   c. Incipient cracking

2. Isostatic pressing

   a. Equilibrium condition
   b. Uniform condition
   c. Non-uniform, internal
   d. External

   1. Pressure used
   2. Vacuum
   3. Hard
   4. Rubber

   a. Oil
   b. Water

   a. Uniform (unified)
   b. Non-uniform
   c. Rubber
   d. Powder
العمليات الجافة في السيراميك:

- عملية الجافة في السيراميك تتطلب تدفق الهواء.
- تتراوح سرعة طبقة الماء حسب الوقت.
- الهواء الذي يمر عبر الطبقة الماء يفقد درجة حرارة.
- درجات حرارة الهواء أثناء الجافة تتناقص.
- الهواء النقي يحمل الماء المذاب.

- الهواء يتمثل في أنه يوفر الحرارة للجفاف.
- يغطي الهواء النقي الجزء السفلي من الماء.

السماح للماء بحمض الجاف:

- ينتشر الماء على سطح السيراميك.
- الهواء يغطي سطح الماء.
- الهواء يرافق الماء المذاب إلى جوف المخلب.

Flow air:
- يوفر حرارة لجفاف الماء.
- يحمل الهواء الماء المذاب.

Flow water:
- حركة الماء.
- سرعة الماء.

تعددت الموارد أدناه مثل نظام أفلام وسادة، حيث يربط بين الماء والمادة.

\[
\frac{\text{dv}}{\text{dt}} = \frac{k}{l} \frac{(C_2 - C_1)}{\eta}
\]

- \(C_1\): تركيز الماء.
- \(C_2\): تركيز الماء في النهاية.
- \(k\): ثابت.
- \(l\): طول المسار.
- \(\eta\): وفرة الماء.
- \(\eta\): سرعة الماء.

العمليات الجافة تعتبر نوعًا من النماذج المائية المتغيرة، حيث يتم تحسين التدفق الجاف للسماح للهواء في التدفق من خلال الماء.
Factors affecting drying processes:

1. Initial moisture content
2. Particle size
3. Amount of non-plastic material in their particle size
4. Temperature of drying
5. Particle pressure of water vapour
6. Velocity of hot air

Drying Rate of Ceramic

dark at point B - why?
light at point C

Drying schedule:
- different materials
- methods of forming
- shape and size of the product

Graphs showing:
- Rate of dry
- % Relative humidity
- Air temperature
- Time
The removal of moisture content using the conditions:

\[ w \]

- The linear drop in relative humidity through period (b) produces almost a linear increase in the drying rate, and this is reflected in the curve of \( w \) down to the c.p. (critical point).

- In time period (c) the falling rate period of water removal from the clay body.

- In stage (a) is for conditioning of the wave where:

  - The product brought up to predetermined temp. with \\
    - linear drying period where shrinkage takes place is \\
    designated as (b). To prevent warping and cracking \\
    gradual drop in humidity, with out increase in temp. \\
    is desirable. About third \( \frac{1}{3} \) of the total \\
    required is devoted to this stage. \\

\[ \text{Time} \]
After the c.p. (shrinkage limit point) is past more drying energy can be applied to the wood without danger of warping and cracking.

Since this is the falling rate period where the removal of the moisture becomes progressively:

- moisture diffusivity is increased in steep--and a decrease
- in relative humidity were in order it takes 8 the total drying time.

اًلْرِيْضَاءُ

تَسْمَعُ عَلَىَّ أَنَّكَ قَدْ أَنْضَجْتَ.

- خَلَأَ لهُمَا (فَطَنِي) بِمَهَبَّةٍ مَّعَ مُرَأَبٍ نِّسَأَتُ غَنْظَيْهُ

- تَسْحَرُوا مَعَكَ بِذُرْعٍ شَوَّيْنَا، ثُمَّ تَسْلُبُوا

- أَنْتُمْ مَنْ قَضَأَتْ سَهْلًا فَيَرَى الْرَّجُلُ، تَسْلُبُوا

- إِنَّكُمْ أَلْحَقُو فِي مَنْ أَنْضَجَ مَعَاً، فَيَرَى الْرَّجُلُ

- لَنْ يَكُونَ لَكُمْ أَمْكَانَ أَنْ يَسْقِعُ فِي رَحْلَةٍ مُّسْتَقِفٍ

- يُقَدِّسُونَ النَّارَةِ.
Firing process:

1. Temperature of firing
2. Type of product
3. Composition of raw material

In solid state reaction, two reacted particles must be in contact when enough energy in the form of heat is applied to make the reaction go.

\[
\log \frac{K_{T_1}}{K_{T_2}} = A \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]

- \(K_{T_1}\): reaction velocity at Temp. \(T_1\)
- \(K_{T_2}\): reaction velocity at Temp. \(T_2\)
- \(A\): constant

A liquid acted as a means of atomic transfer.

In solid state reaction for one component (e.g., MgO from MgCO\(_3\)) a crystal growth occurs due to breaking of atomic bonds by thermal energy.
so that the free atoms or atom groups tend to fall on the larger crystals that have greater surface energy. Therefore the small crystals grow smaller and the large crystal grow larger.

\[ \log R = \log R_0 - n \log t \]

\[ R = R_0 / t^n = \frac{31}{t^{1/5}} \]

- \( R \): rate of growth in Angstroms/sec.
- \( n \): slope of strength line
- \( t \): time in sec.

Can be called grain growth - increase in size of CaO particles.

\[ \text{CaO particles} \Rightarrow \text{CaSiO}_4 \text{ particles} \]

\[ \text{reaction layer } \frac{dN}{dt} \text{ diffusion of cations} \]

\[ \frac{dy}{dt} = k/y \]

- \( y \): thickness of the product layer
- \( t \): time
- \( k \): reaction rate constant.

This relation says that the rate of growth of product layer is inversely proportional to its thickness.

\[ y^2 = 2k + \text{integrating form of the above equation} \]
The rate of high-temperature reactions is of great particle concern in the industry.

the increase in rates with temp. is expressed by an equation:

\[ \frac{dl_n k}{dt} = \frac{E_a}{RT^2} \]

Arrhenius' Equation

\( k \) = reaction constant  
\( T \) = Temp. (absolute)  
\( E_a \) = Activation energy  
\( R \) = Gas Constant.

\[ k = A \exp \left( -\frac{E_a}{RT} \right) \]

\( A \) = integration Constant

From this equation it seems that the extent of reaction per mole in a unit of time is inversely proportional to the exponential of the activation energy and directly proportional to the exponential of temp.

Ceramic sintering (Density increase)

Sintering: is the processes where by a heat treatment is used to convert a powder compaction into a dense polycrystalline solid.
**Process of Sintering**

1. **Initial Stage:**
   a) With time there is an increase in inter-particle contact area.
   b) Sharp angles at the points of contact are rounded off.
   c) In many cases the powder particle centers approach each other, but in not all unit as many cases the particle powder centers do not move.

2. **Intermediate Stage:**
   - Nearly all pores are interconnected, but with time they decrease in volume.
   - At longer times the pores become broken into isolated pores.

3. **Final Stage:**
   - Grain growth and grain boundary area decrease.
   - Isolated pores decrease in volume giving the final increase in density.
The transfer of material is by:

1. Viscous flow
2. Plastic flow
3. Evaporation-Condensation
4. Volume diffusion
5. Surface diffusion
6. Solution-precipitation

1, 2, 3 Contact area increased with simultaneous approach of centers.

4, 5, 6 Inter-particle neck growth with end center approach.

Three broad categories of thermal consolidation (Types of sintering process):

1. Solid State Sintering:

   - High purity Ceramics (high purity materials)
2. Liquid phase sintering:

The method involves the use of a liquid phase to aid in the sintering process. This is accomplished by adding a liquid to the powder mixture, which helps to reduce the interparticle forces and allows for easier sintering.

3. Viscous Flow sintering:

This method involves the use of a liquid phase that flows under the influence of gravity to aid in the sintering process. The liquid phase helps to fill in voids in the powder mixture, facilitating easier sintering.

Driving force for sintering:

1. Macrotropic. It is the free energy decrease that occurs when substantial area of the original powder - vapour interface is removed.

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1. Macrotropic. It is the free energy decrease that occurs when substantial area of the original powder - vapour interface is removed.
Ex. when 1 kg of 1mm diameter spherical powder with surface energy 0.88 J m\(^{-2}\) and density \(4.5 \times 10^3\) kg m\(^{-3}\) is used to form a single large sphere, the energy change is estimated as flow, energy is reduced by an amount equal to the original surface energy of the powder:

\[
\text{All} = \frac{\text{energy}}{\text{mass}} = \frac{\text{energy}}{\text{area}} \times \frac{\text{area}}{\text{particle}} \times \frac{\text{particle}}{\text{volume}} \times \frac{\text{volume}}{\text{mass}} \times \frac{\text{mass}}{\text{unit}}
\]

\[
\text{Area} = 4\pi r^2 = \frac{6}{\sqrt{13}} \times \frac{4.5 \times 10^3}{1 \times 10^{-6}} \times \frac{1}{\rho}
\]

\[
\rho = 0.56 \text{ KJ Kg}^{-1}
\]

For hard powder for example taking a theoretical reaction (400 KJ mol\(^{-1}\)) as being typical

\[
\frac{\text{energy}}{\text{mol}} = \frac{\text{energy}}{\text{area}} \times \frac{\text{area}}{\text{particle}} \times \frac{\text{particle}}{\text{volume}} \times \frac{\text{volume}}{\text{mass}} \times \frac{\text{mass}}{\text{unit}}
\]

\[
= \frac{6}{\sqrt{13}} \times \frac{4\pi r^2}{4.5 \times 10^3} \times \frac{1}{\rho} \times \frac{M}{M}
\]

For molar mass say 0.04 kg mol\(^{-1}\) these can be put equal to 400 KJ mol\(^{-1}\)

\[
400 \times 10^3 = \frac{M}{\rho} \times \frac{0.04}{4.5 \times 10^3} = 0.04
\]

\[
M = 5.6 \times 10^{-11}\text{ m}^3\text{ on which the atomic dimension}
\]
Microscopic driving force: It is due to the pressure difference that exists at equilibrium across a curved surface.

Ex: Spherical cavity 1 cm, surface energy 1.96 J/m.

The total surface energy of the pore wall is reduced if the pore shrinks. However, the gas pressure inside the pore would increase, and to maintain the pore at an equilibrium size of 1 cm we can consider that the gas pressure increase must be

\[ \rho \Delta V = \gamma \Delta A \]

\( \rho \): pressure difference across the surface.

\( \Delta V \): pore volume change.

\( \gamma \): surface energy,

\( \Delta A \): pore surface area change for sphere

\[ V = \frac{4}{3} \pi r^3 \]

\[ \frac{dV}{dr} = 4 \pi r^2 \]

\[ A = 4 \pi r^2 \]

So

\[ \frac{dA}{dr} = 8 \pi r \]
\[ \rho \cdot 4 \pi r^2 dr = \rho \left( r \right) dV \]

\[ \rho = \frac{\alpha \cdot 2 \cdot \pi \cdot r^2 \cdot dr}{1 \cdot 10^{-6}} = 3 \cdot 2 \cdot 10^6 \text{ Jm}^{-3} \]

which is approximately 20 atmospheres.

\[ \rho = \frac{\alpha \cdot 2 \cdot \pi \cdot r^2 \cdot dr}{1 \cdot 10^{-6}} \]

\[ \alpha = 2 \text{ for sphere} \]

\[ \alpha = 1 \text{ for cylinder} \]

Solid state sintering

- High Temperature strength.

- No liquid phase in this process at any stage.

- Densification is achieved by change in particle shape with no contribution from re-arrangement of the pores.

- Two routes exist by which the compact grains can use the macroscopic driving force.
1. Densification

In which particle remains at their original size but γ is replaced by grain boundary energy \( \gamma_{gb} \), while each powder particle change its shape.

2. Coarsening

Particle grain retain their original shape but grow large and hence reduce \( \gamma_{gb} \).

\[ x = \left( \frac{\pi}{2} \right)^{1/6} \left( \frac{M}{kT} \right)^{1/2} \left( \frac{3 \gamma_{gb}}{d^2} \right)^{1/3} \]

where growth

\[ n \left( \frac{x}{L} \right)^5 \left( \frac{x}{L} \right)^2 \left( \frac{M}{kT} \right)^{3/2} \]

\[ L = \frac{x}{2r} \quad \text{radius of lens} \]

\[ v = \frac{\pi x^3}{2r} \quad \text{volume of the lens} \]
neck growth between particles

\[ \frac{x}{y} \]

surface tension

\[ \gamma \]

molecular weight of the vapour

\[ \mu \]

density of the material

\[ \rho \]

increased by decreasing the grain size and by increasing the time

\[ \frac{x}{y} \]

diffusion

material transfer by diffusion

\[ X^2 = K_1 \frac{y a^2 D_s}{K_T} \cdot r^m \cdot t \]

\[ D_s \]

d through of guality

\[ \frac{\Delta L}{L} \]

linear shrinkage

\[ (\Delta L/L) = K_2 \frac{y a^3 D_s}{K_T} \cdot r^{5.5} \cdot t \]

\[ k, m, k_1, k_2, a, D_s \]

are constants depends on type of diffusion (example: surface diffusion, volumetric diffusion, contact surface diffusion).