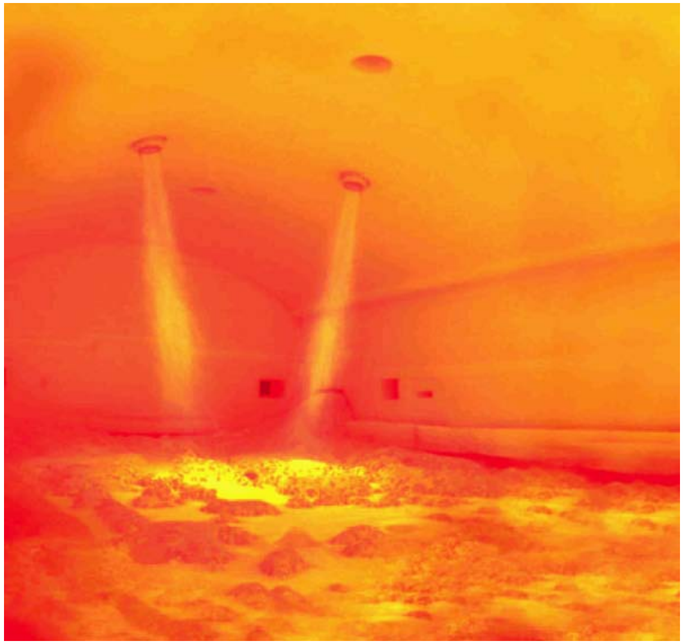
Chapter 2 Glass Melting and Glass Forming

Introduction

The majority of glasses are produced by melting batch components at high temperature.

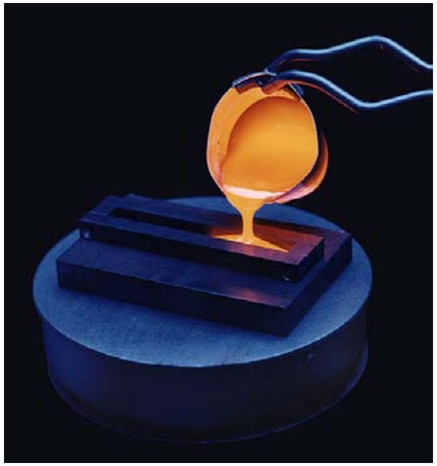
This procedure involves:

selection of raw materials
calculation of the amounts of raw materials needed
weighing and mixing the raw materials
melting
removal of unmelted batch, impurities and bubbles
cooling and shape forming
heat treatments (annealing, tempering)



Inside of a furnace

Glass bottle forming



Laboratory glassmaking

General Flow of Glass Manufacture

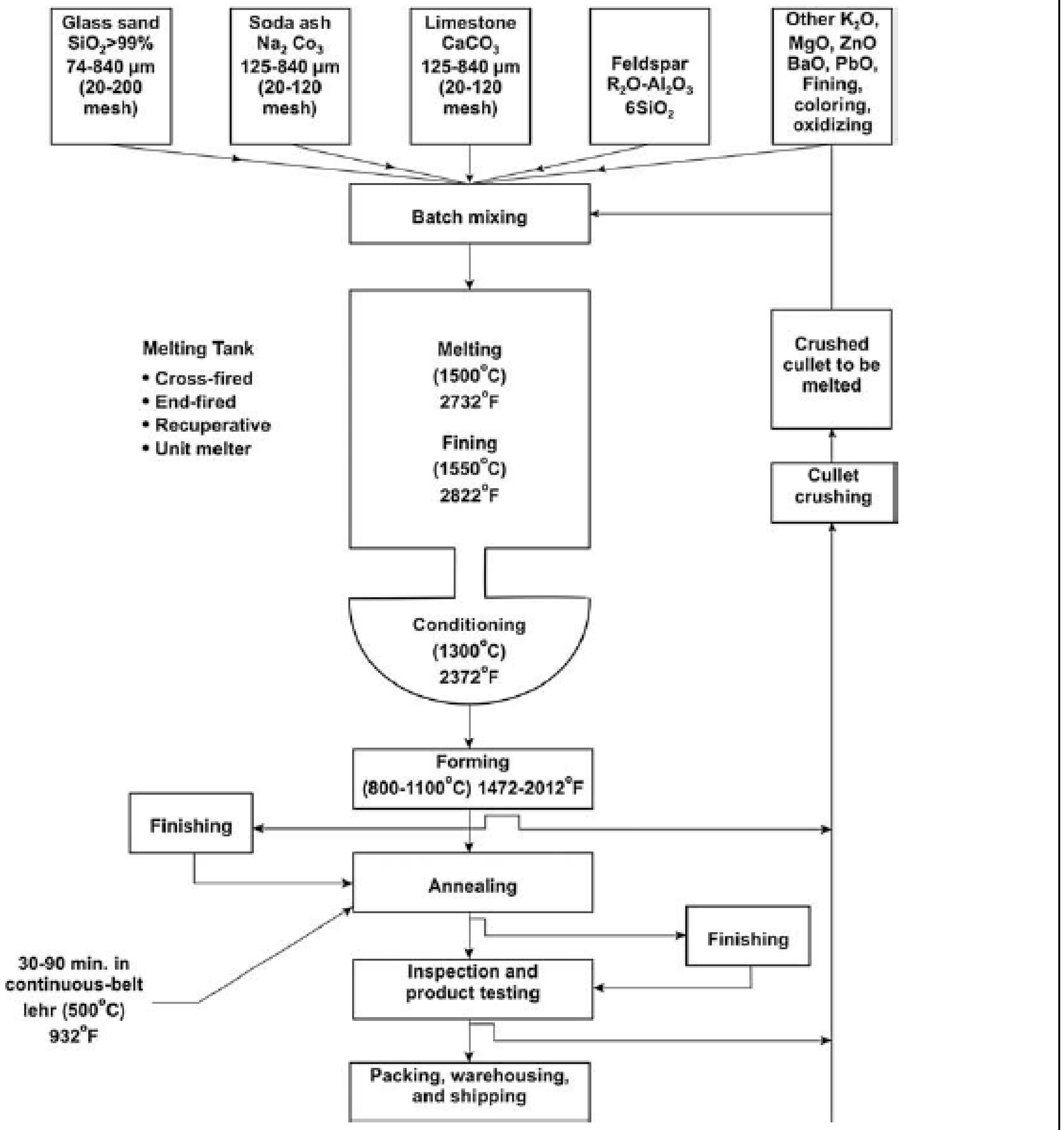


Figure A.1

Raw Materials

Research glasses, optical glasses, high-performance glasses: high purity chemicals

Window glasses, container glasses: minerals (usually low purity)

Batch materials can be divided into 5 types:

glassformer

flux

property modifier

colorant

fining agent

The same compound may be placed in more than one catagory

e.g. Al_2O_3 is a glassformer in aluminate glasses, but a property modifier in silicate glasses

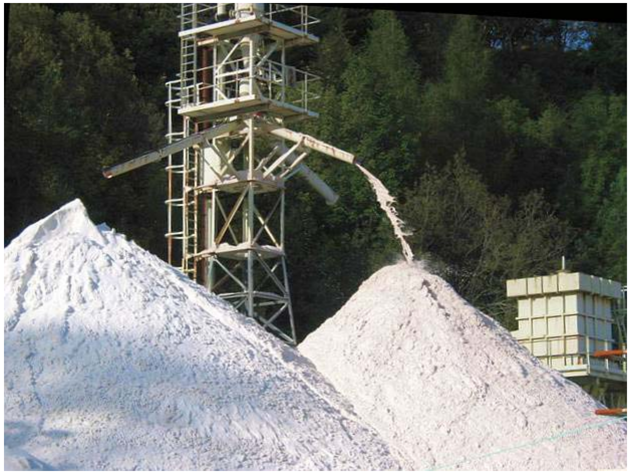
As_2O_5 can be a glassformer or a fining agent.

The most important component of any glass batch is the glassformer (also called network former or glassforming oxide). Primary glassformers in commercial oxide glasses:

SiO_2 (silica)
B_2O_3 (boric oxide)
P_2O_5 (phosphoric oxide)

} form single component glasses

GeO_2 also forms a single component glass.



Some oxides can be glassformers when mixed with other oxides: e.g. As_2O_5, Bi_2O_3, Ga_2O_3, Al_2O_3, TeO_2, V_2O_5.

Silicate glasses

- Most commercial glasses use SiO_2 as the glassformer.
- SiO_2 forms an excellent glass but has a high melting temperature (>2000°C).
- For window and container glass, *fluxes* are added to reduce the melting temperature to below 1600°C.
- Common fluxes: alkali oxides (usually Na_2O or K_2O), PbO.
- PbO is very good at dissolving impurities (e.g. refractory particles) but is toxic.
- Addition of alkali oxides causes degradation of many properties, especially chemical resistance.
- This degradation can be reduced by using *property modifiers* e.g. alkaline earth oxides, transition metal oxides, alumina.
- These oxides cause a small increase in processing temperatures, but improve glass properties.
- *Colorants* are added to control the colour of the glass.
- Usually oxides of 3d transition metals or 4f rare earths.
- Gold and silver can also produce colours by formation of colloids in glasses.
- Iron oxides (impurities in sands) are often unintentional colorants.
- *Decolorants* can be added to counteract the effect of other colorants.
- *Fining agents* are added to remove bubbles from the melt.
- Include As_2O_5, Sb_2O_3, NaCl, CaF_2, NaF, Na_3AlF_6 and some sulfates.
- Added in very small amounts (< 1 wt %).

Compositional Nomenclature

Oxide Glasses

- Compositions can be expressed in weight, molar or atomic fractions.
- Historically, compositions were expressed in *weight percentages* of the oxide components.
- E.g. a soda-lime-silica glass may have composition 15 % soda, 10 % lime and 75 % silica
- This is useful for commercial production, but not for laboratory studies.
- Modern literature uses *molar percentages*.
- Useful for understanding effects of composition on properties, but complicates batch preparation.

Atomic fractions

- Used for chalcogenides and simple oxide glasses.
- E.g. a glass with 40 atom % arsenic and 60 atom % sulphur can have the formulae As_2S_3, $As_{40}S_{60}$ or $As_{0.4}S_{0.6}$.
- For oxides, things can get confusing.
- E.g. the system x Li_2O - (100 - x) SiO_2, where glasses can be made for $0 < x < 40$.
- Using the atom % approach, we get the general formula $Li_{2x}Si_{(100-x)}O_{(200-x)}$.
- A glass with x = 33.33 can be written as 33.33 Li_2O - 66.66 SiO_2, $Li_{66.7}Si_{66.7}O_{166.7}$, Li_2O-$2SiO_2$ or $Li_2Si_2O_5$.

Remember, the glass doesn't contain structural units of the oxides or atomic formulae.

Halide Glasses

- ZrF_4 - based heavy metal fluoride glasses are designated with an acronym which lists the glassformer first.
- Remaining components are listed in order of ascending cation valence (but monovalent cations are listed last).
- To make things worse, elements are not designated by their normal chemical symbols.
- E.g. a glass with ZrF_4, BaF_2, AlF_3, LaF_3 and NaF is a ZBLAN glass.
- A glass containing Li instead of Na would be a ZBLALi glass.
- For other halide glasses, things become more confusing.
- E.g. a system containing Cd, Li, Al and Pb is labelled CLAP rather than CLiAP.

Batch Calculations

All batch calculations follow the same procedure:

1. Multiply the mole fraction of each component by its molecular weight.
2. Total these contributions to get the molecular weight of the glass.
3. Divide each contribution by the molecular weight of the glass to get the weight fraction of each component.
4. Multiply the weight fraction of each component by the amount of glass to be produced.

If a component decomposes during melting e.g. Na_2CO_3, its batch weight is adjusted by multiplying the weight fraction of that component by the gravimetric factor for the raw material used in the batch.

Some raw materials supply more than one component e.g. albite feldspar Na_2O-Al_2O_3-$6SiO_2$

Small compositional changes are often excluded from batch calculations.
E.g. we may add 0, 0.1, 0.2 or 0.5 wt % As_2O_5 to a base soda-lime-silica composition.
The molar composition of the glass changes slightly as As_2O_5 is added.
This is not acceptable for large additions i.e. > 1 wt %.

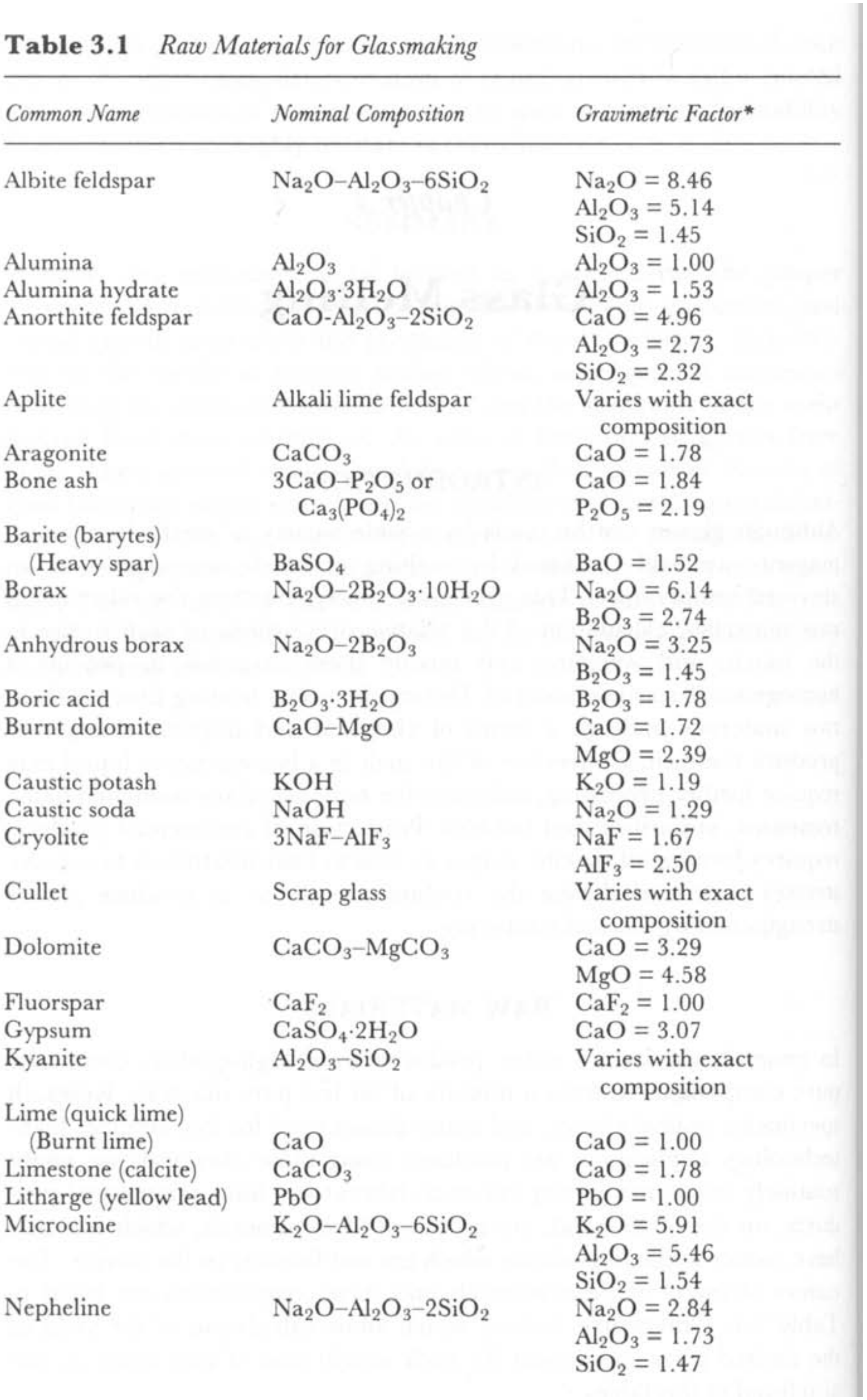
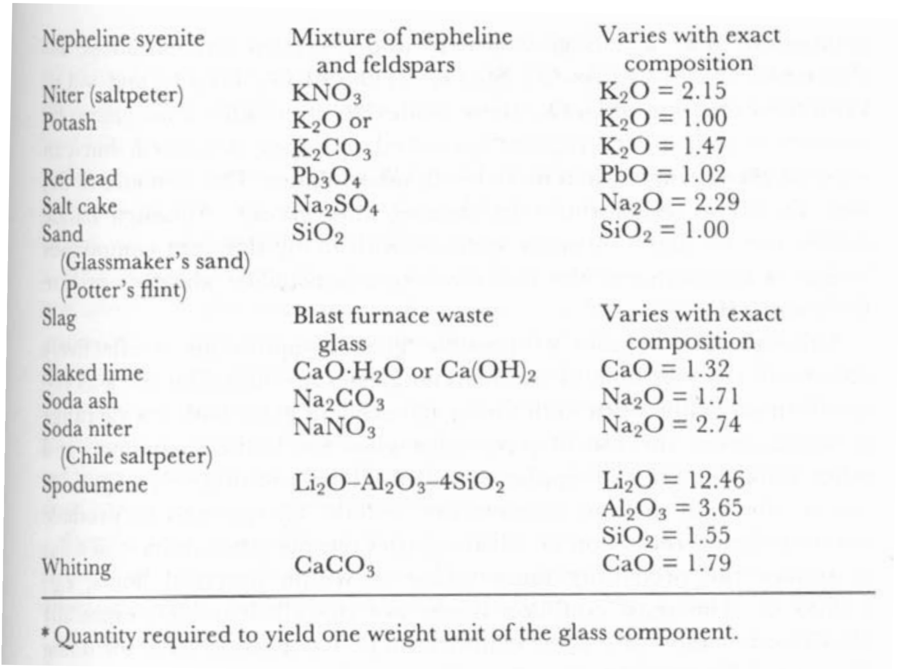
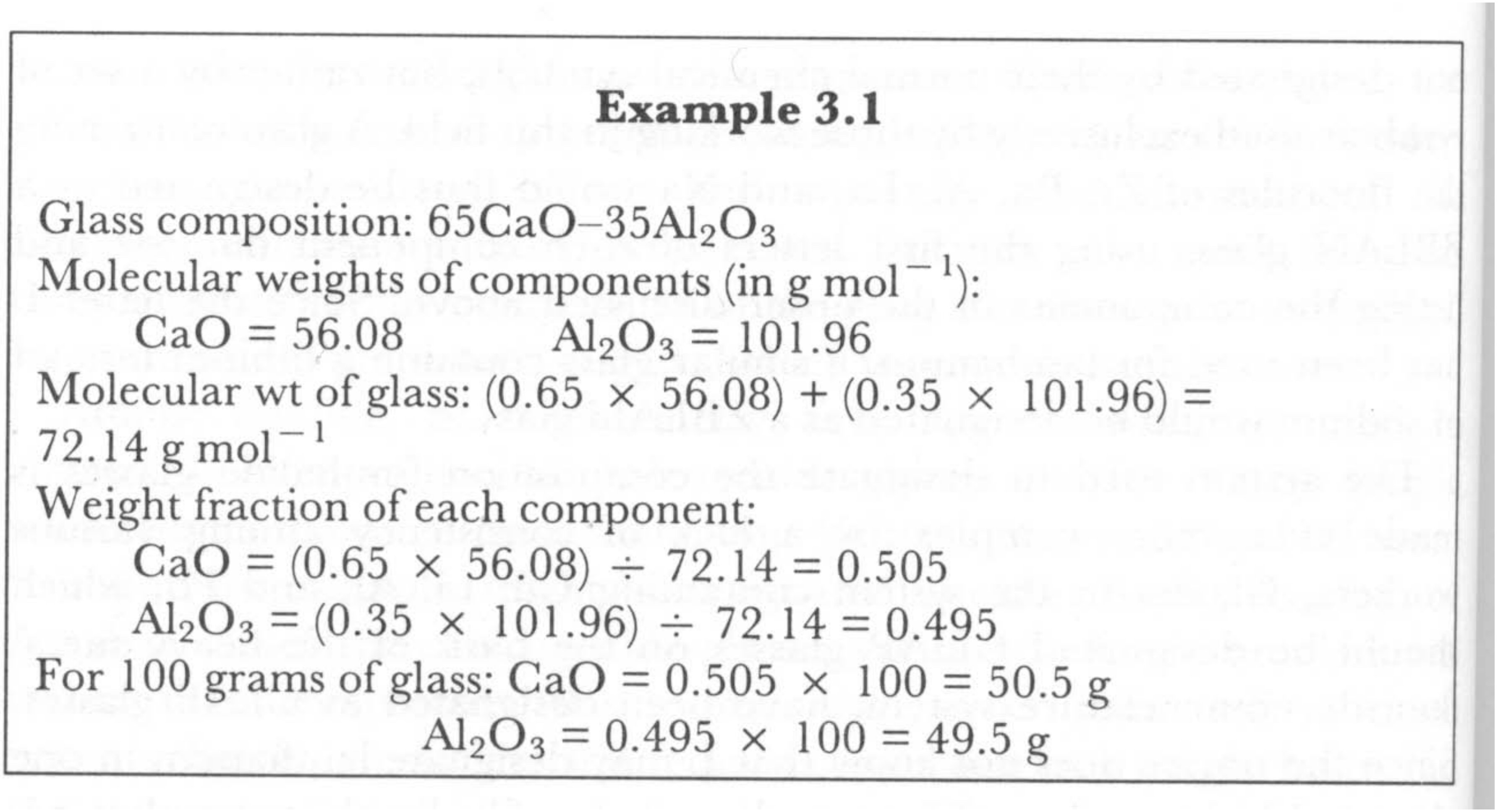


Table 3.1 *Raw Materials for Glassmaking*

Common Name	*Nominal Composition*	*Gravimetric Factor**
Albite feldspar	$Na_2O–Al_2O_3–6SiO_2$	$Na_2O = 8.46$ $Al_2O_3 = 5.14$ $SiO_2 = 1.45$
Alumina	Al_2O_3	$Al_2O_3 = 1.00$
Alumina hydrate	$Al_2O_3 \cdot 3H_2O$	$Al_2O_3 = 1.53$
Anorthite feldspar	$CaO\text{-}Al_2O_3–2SiO_2$	$CaO = 4.96$ $Al_2O_3 = 2.73$ $SiO_2 = 2.32$
Aplite	Alkali lime feldspar	Varies with exact composition
Aragonite	$CaCO_3$	$CaO = 1.78$
Bone ash	$3CaO–P_2O_5$ or $Ca_3(PO_4)_2$	$CaO = 1.84$ $P_2O_5 = 2.19$
Barite (barytes) (Heavy spar)	$BaSO_4$	$BaO = 1.52$
Borax	$Na_2O–2B_2O_3 \cdot 10H_2O$	$Na_2O = 6.14$ $B_2O_3 = 2.74$
Anhydrous borax	$Na_2O–2B_2O_3$	$Na_2O = 3.25$ $B_2O_3 = 1.45$
Boric acid	$B_2O_3 \cdot 3H_2O$	$B_2O_3 = 1.78$
Burnt dolomite	$CaO–MgO$	$CaO = 1.72$ $MgO = 2.39$
Caustic potash	KOH	$K_2O = 1.19$
Caustic soda	$NaOH$	$Na_2O = 1.29$
Cryolite	$3NaF–AlF_3$	$NaF = 1.67$ $AlF_3 = 2.50$
Cullet	Scrap glass	Varies with exact composition
Dolomite	$CaCO_3–MgCO_3$	$CaO = 3.29$ $MgO = 4.58$
Fluorspar	CaF_2	$CaF_2 = 1.00$
Gypsum	$CaSO_4 \cdot 2H_2O$	$CaO = 3.07$
Kyanite	$Al_2O_3–SiO_2$	Varies with exact composition
Lime (quick lime) (Burnt lime)	CaO	$CaO = 1.00$
Limestone (calcite)	$CaCO_3$	$CaO = 1.78$
Litharge (yellow lead)	PbO	$PbO = 1.00$
Microcline	$K_2O–Al_2O_3–6SiO_2$	$K_2O = 5.91$ $Al_2O_3 = 5.46$ $SiO_2 = 1.54$
Nepheline	$Na_2O–Al_2O_3–2SiO_2$	$Na_2O = 2.84$ $Al_2O_3 = 1.73$ $SiO_2 = 1.47$
Nepheline syenite	Mixture of nepheline and feldspars	Varies with exact composition
Niter (saltpeter)	KNO_3	$K_2O = 2.15$
Potash	K_2O or K_2CO_3	$K_2O = 1.00$ $K_2O = 1.47$
Red lead	Pb_3O_4	$PbO = 1.02$
Salt cake	Na_2SO_4	$Na_2O = 2.29$
Sand (Glassmaker's sand) (Potter's flint)	SiO_2	$SiO_2 = 1.00$
Slag	Blast furnace waste glass	Varies with exact composition
Slaked lime	$CaO \cdot H_2O$ or $Ca(OH)_2$	$CaO = 1.32$
Soda ash	Na_2CO_3	$Na_2O = 1.71$
Soda niter (Chile saltpeter)	$NaNO_3$	$Na_2O = 2.74$
Spodumene	$Li_2O–Al_2O_3–4SiO_2$	$Li_2O = 12.46$ $Al_2O_3 = 3.65$ $SiO_2 = 1.55$
Whiting	$CaCO_3$	$CaO = 1.79$



*Quantity required to yield one weight unit of the glass component.



Example 3.1

Glass composition: $65CaO{-}35Al_2O_3$

Molecular weights of components (in g mol^{-1}):

$CaO = 56.08$ $Al_2O_3 = 101.96$

Molecular wt of glass: $(0.65 \times 56.08) + (0.35 \times 101.96) = 72.14$ g mol^{-1}

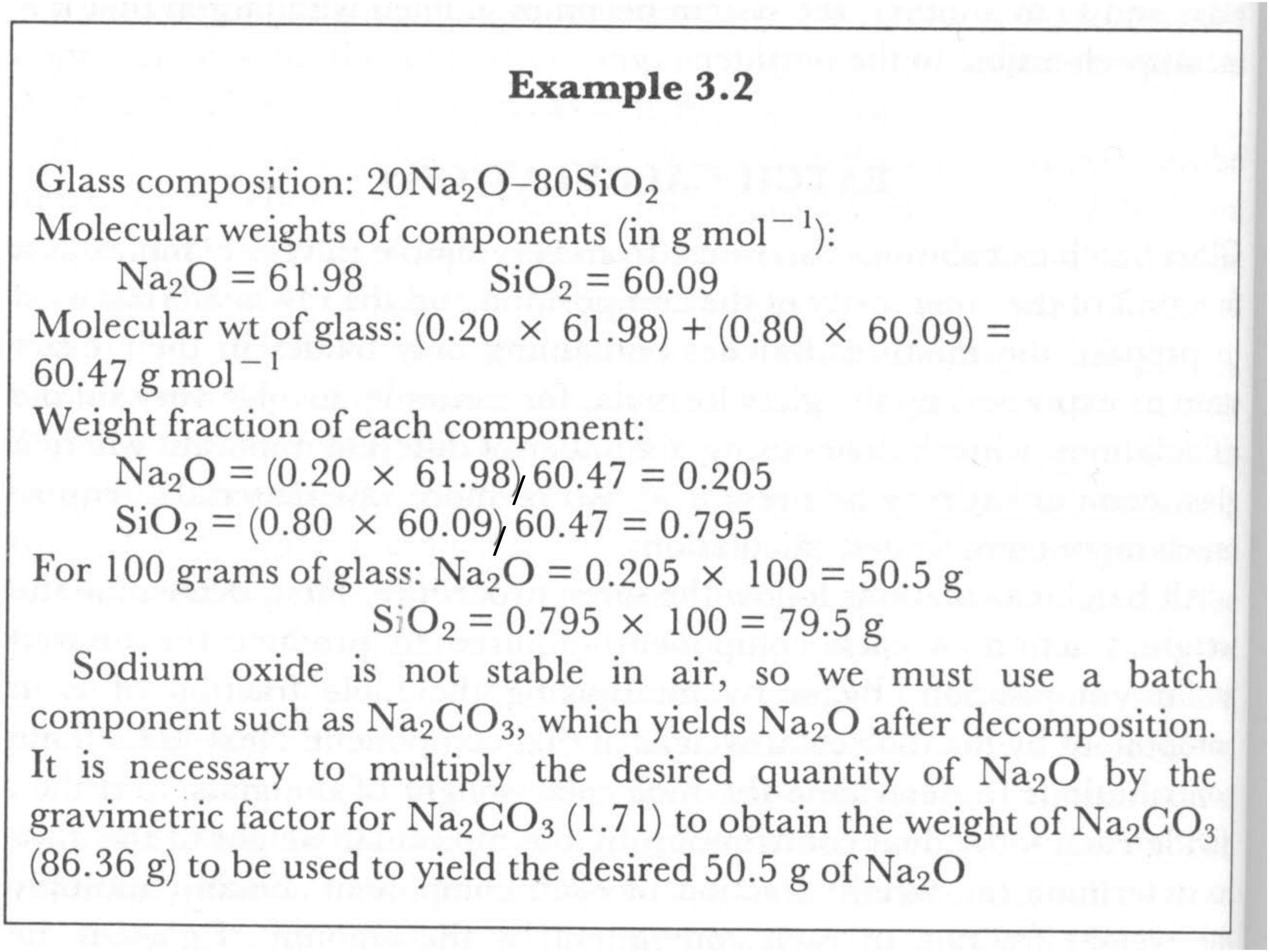
Weight fraction of each component:

$CaO = (0.65 \times 56.08) \div 72.14 = 0.505$

$Al_2O_3 = (0.35 \times 101.96) \div 72.14 = 0.495$

For 100 grams of glass: $CaO = 0.505 \times 100 = 50.5$ g

$Al_2O_3 = 0.495 \times 100 = 49.5$ g

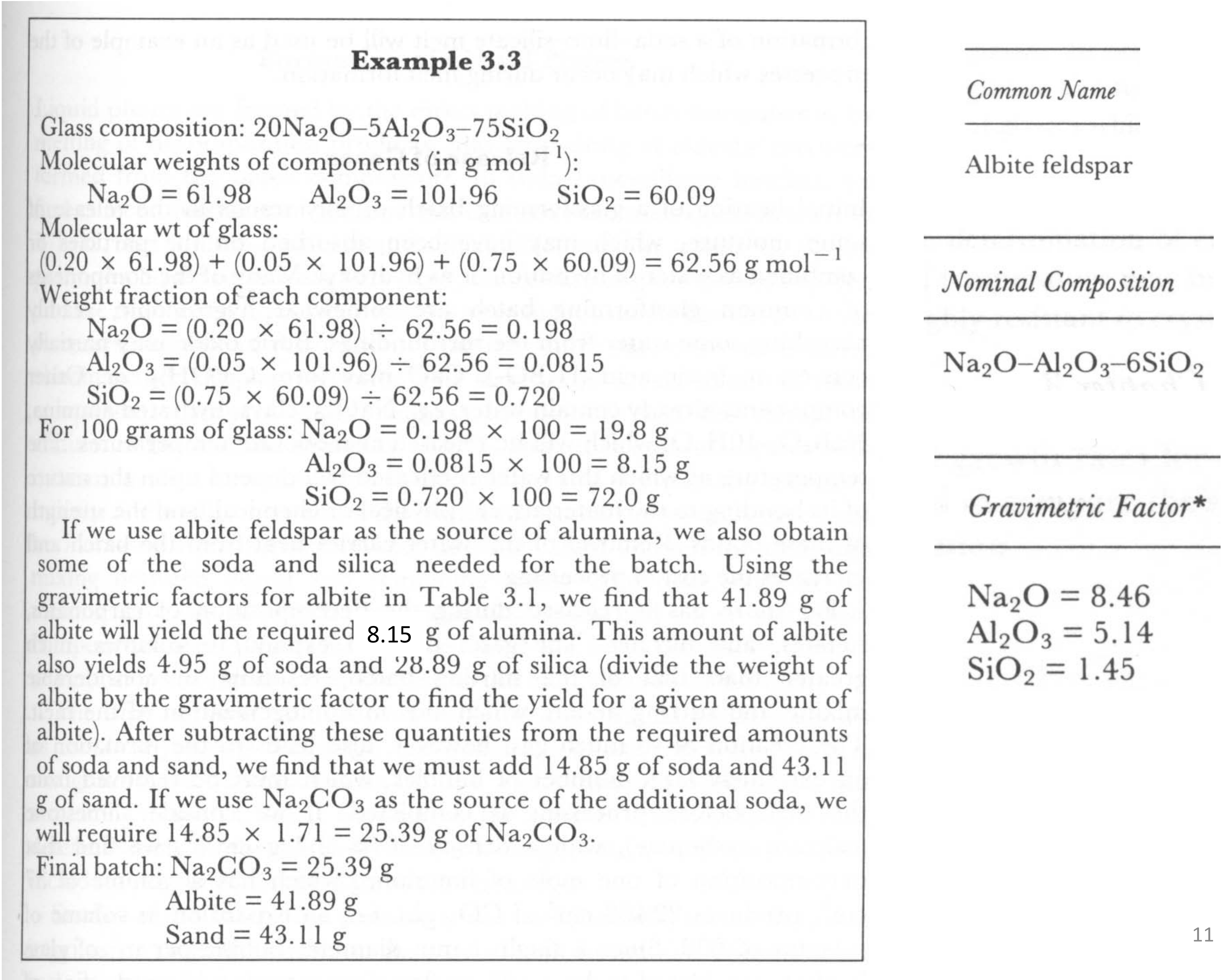


Example 3.2

Glass composition: $20Na_2O–80SiO_2$
Molecular weights of components (in g mol^{-1}):
$Na_2O = 61.98$ $SiO_2 = 60.09$
Molecular wt of glass: $(0.20 \times 61.98) + (0.80 \times 60.09) = 60.47$ g mol^{-1}
Weight fraction of each component:
$Na_2O = (0.20 \times 61.98)/60.47 = 0.205$
$SiO_2 = (0.80 \times 60.09)/60.47 = 0.795$
For 100 grams of glass: $Na_2O = 0.205 \times 100 = 50.5$ g
$SiO_2 = 0.795 \times 100 = 79.5$ g

Sodium oxide is not stable in air, so we must use a batch component such as Na_2CO_3, which yields Na_2O after decomposition. It is necessary to multiply the desired quantity of Na_2O by the gravimetric factor for Na_2CO_3 (1.71) to obtain the weight of Na_2CO_3 (86.36 g) to be used to yield the desired 50.5 g of Na_2O

RMM $Na_2O = 61.978$ RMM $Na_2CO_3 = 105.989$ Gravimetric factor = RMM $Na_2CO_3 \div$ RMM $Na_2O = 1.710$



Example 3.3

Glass composition: $20Na_2O–5Al_2O_3–75SiO_2$

Molecular weights of components (in g mol^{-1}):

$Na_2O = 61.98 \quad Al_2O_3 = 101.96 \quad SiO_2 = 60.09$

Molecular wt of glass:

$(0.20 \times 61.98) + (0.05 \times 101.96) + (0.75 \times 60.09) = 62.56$ g mol^{-1}

Weight fraction of each component:

$Na_2O = (0.20 \times 61.98) \div 62.56 = 0.198$

$Al_2O_3 = (0.05 \times 101.96) \div 62.56 = 0.0815$

$SiO_2 = (0.75 \times 60.09) \div 62.56 = 0.720$

For 100 grams of glass: $Na_2O = 0.198 \times 100 = 19.8$ g

$Al_2O_3 = 0.0815 \times 100 = 8.15$ g

$SiO_2 = 0.720 \times 100 = 72.0$ g

If we use albite feldspar as the source of alumina, we also obtain some of the soda and silica needed for the batch. Using the gravimetric factors for albite in Table 3.1, we find that 41.89 g of albite will yield the required 8.15 g of alumina. This amount of albite also yields 4.95 g of soda and 28.89 g of silica (divide the weight of albite by the gravimetric factor to find the yield for a given amount of albite). After subtracting these quantities from the required amounts of soda and sand, we find that we must add 14.85 g of soda and 43.11 g of sand. If we use Na_2CO_3 as the source of the additional soda, we will require $14.85 \times 1.71 = 25.39$ g of Na_2CO_3.

Final batch: $Na_2CO_3 = 25.39$ g

Albite = 41.89 g

Sand = 43.11 g

Common Name	*Nominal Composition*	*Gravimetric Factor**
Albite feldspar	$Na_2O–Al_2O_3–6SiO_2$	$Na_2O = 8.46$ $Al_2O_3 = 5.14$ $SiO_2 = 1.45$

Mechanisms of Batch Melting

- The following steps occur during batch melting:

1. release of gases
2. formation of liquid phases
3. removal of bubbles (fining)

- Soda-lime-silica melt example.

Release of gases

- Initial heating removes moisture (adsorbed water, water of hydration, hydroxyl groups).
- Many batch components are hygroscopic e.g. $B_2O_3 + 3H_2O \rightarrow 2H_3BO_3$

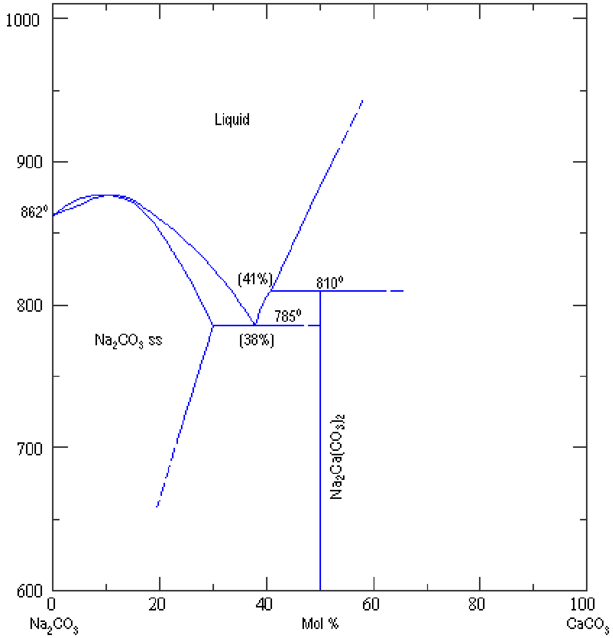
  $CaO + H_2O \rightarrow Ca(OH)_2$
- Some components already contain water e.g. $NaOH$, $NaB_4O_7 \cdot 10H_2O$
- Temperature of water release depends on bonding e.g. physical, chemical.
- Removal of water cause heat losses and increases processing costs.
- Much more gas is released during decomposition of carbonates, sulphates and nitrates.
- This gas mixes and stirs the melt, helping homogenization.
- But this gas forms bubbles in the melt which must be removed.
- E.g. 1 mole $CaCO_3$ (density 2.7 $g.cm^{-3}$, volume 37 cm^3) forms 22400 cm^3 of CO_2.
- A single 1mm^3 diameter bubble per m^3 of glass is a serious flaw in commercial glasses.
- Rapid liquid formation can entrap air between unmelted particles.
- This air can expand and cause foaming of the melt.
- Never fill a crucible to the top with batch.

Formation of liquid phases

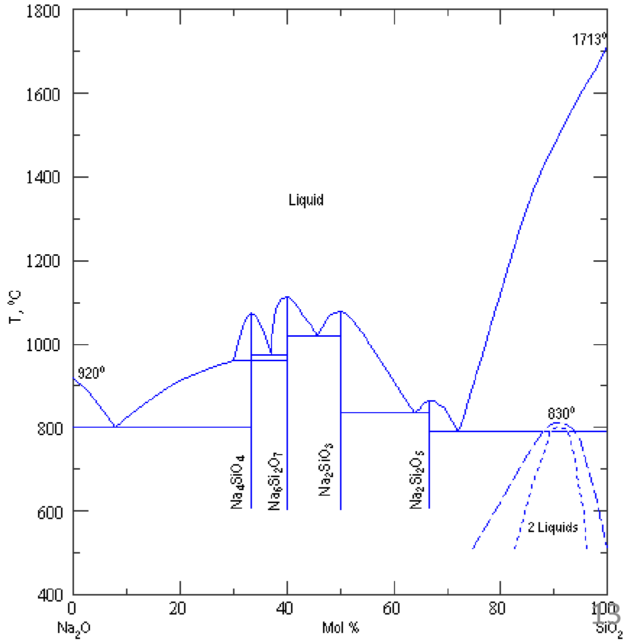
Liquid phases formed by:

1. direct melting of batch components
2. melting of decomposition products
3. melting of eutectic mixtures

E.g. Na_2CO_3 and $CaCO_3$ - eutectic at 775°C
$Na_2Si_2O_5$ and SiO_2 - eutectic at ~800°C

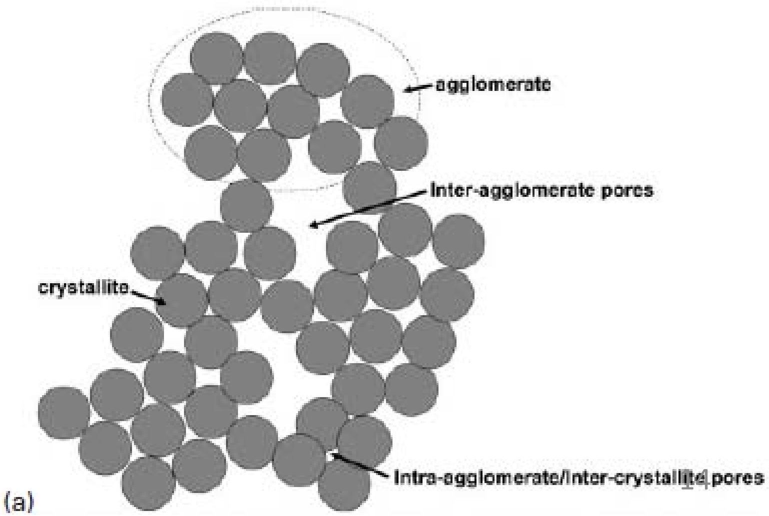


- Liquid phases at this stage are fluid, gas is rapidly released and the liquid/solid mixture is turbulent.
- As temp increases, refractory particles e.g. SiO_2, Al_2O_3 dissolve.
- Melt viscosity increases rapidly and more gases are released (CO_2 solubility in melt decreases as SiO_2 concentration in melt increases).
- Temp must be increased further to lower viscosity and allow continued mixing of liquid and solids.
- Final stage - remaining SiO_2 dissolves and melt composition homogenizes (becomes uniform) - slow due to high melt viscosity.
- ***Batch-free time***: the time needed to completely dissolve the batch.



- Batch-free time depends on melt composition.
- Simple oxide mixtures often form eutectic mixtures which melt very quickly e.g. CaO - Al_2O_3 glasses
- Many non-silicate melts have low viscosity and rapidly dissolve batch particles.
- Borate, phosphate and germanate melts can be formed at lower temp than silicate melts.
- Batch components can be supplied from different raw materials, which may have different melting temperatures.

  E.g. Al_2O_3 mpt 2072°C nepheline Na_2O-Al_2O_3-$2SiO_2$ mpt 1526°C
- *Batch segregation* separates components which might form eutectic mixtures.
- *Batch mixing* reduces melting temperature and time and improves homogeneity.
- Changes in *particle size* can greatly affect batch-free time.
- Fine particles melt rapidly, but can also agglomerate (form porous clumps).
- The liquid cannot penetrate these agglomerates.
- Agglomerates have low density and can float to the melt surface, which slows dissolution.
- Escape of gases is slowed down due to narrow pore channels.



Melting Accelerants

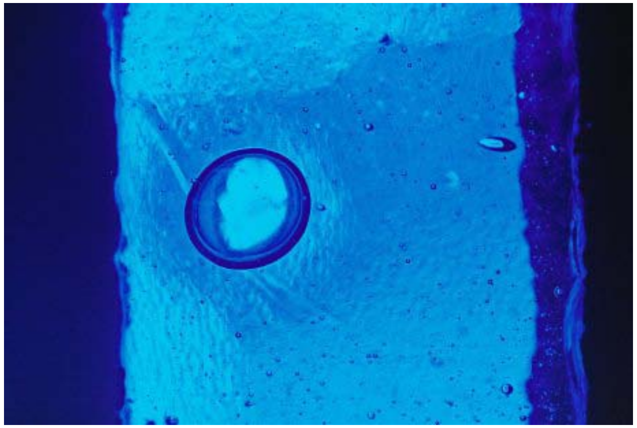
- Replace part of the Na_2CO_3 with compounds which form lower temperature eutectics or fluid melts.
- Na_2SO_4 forms low melting point eutectics and speeds up SiO_2 dissolution.
- Release of SO_3 causes vigorous stirring.
- NaCl forms a eutectic with Na_2CO_3 at 636°C and a fluid liquid.
- Halides in the melt will exchange with oxygen in the atmosphere.
- H_2O also reduces melt viscosity, reducing batch-free time.
- Water can be provided by wetting the initial batch, using H_3BO_3 instead of B_2O_3 or NaOH instead of Na_2CO_3.
- Compaction of batch materials into bricks or pellets increases melting rate by increasing the contact area between particles and improving heat transfer.

Volatilization of Components from Melts

- Many glass components are volatile at high temperature.
- Examples: alkali oxides, lead, boron, phosphorous
- Prolonged melting can significantly change the glass composition due to volatilization.
- Alkali loss increases in the order Li < Na < K < Rb < Cs
- Component volatilization can be reduced by: covering the melt
  lowering melt temperature
- Excess concentration of volatile components can be added to the melt.

- Control of volatilization is used in the commercial production of glasses, but often ignored in laboratory studies.
- Laboratory melts are often held at temperatures and times in excess of those needed to get a homogeneous, bubble-free glass.
- Actual glass composition can be very different from intended composition.
- Actual glass composition can be determined by chemical analysis (expensive) or by measuring weight loss.
- ~0.1 wt % loss is expected from laboratory production of a soda-lime-silica glass.
- up to 20 % wt loss can be observed for melts containing rubidium, caesium or thallium.

Fining of Melts



Fining / refining: the removal of gas bubbles from the melt.

Seed: bubbles < 0.4 mm diameter. Often occur in clusters.

Bubbles: bubbles > 0.4 mm diameter.

- Both are flaws in commercial products.
- Fining begins during batch melting but extends a considerable time after the batch-free time.

Sources of bubbles

- Trapping of air in the batch during initial melting.
- Decomposition of batch components.
- Trapping of air is enhanced by the use of fine sand, or batch components fo very different particle sizes.
- Batch agglomeration is very good at trapping air.
- Mechanical stirring of the melt can force air into the melt.
- Decomposition of batch materials can form large amounts of CO_2, SO_3, NO_x, H_2O, etc.
- Residual carbon in refractories can react with the melt to form CO_2 or CO.

Supersaturation / precipitation

- Many gases have a large enthalpy of solution in glassforming melts.
- Gas solubility in the melt is a strong function of temperature.
- If a species changes its chemical form with changes in temperature or melt composition, it is particularly susceptible to precipitation from melts.
- E.g. Carbon dioxide is present in SiO_2 - rich melts as CO_2 molecules.
- In alkali-rich melts, carbon dioxide forms CO_3^{2-} species with higher solubility.
- During early batch melting, melt is alkali-rich, with high CO_3^{2-} solubility.
- As more SiO_2 dissolves, CO_3^{2-} turns to CO_2, which has lower solubility. CO_2 bubbles form in the melt.

Sulphur: sulphur solubility is sensitive to oxidation state of melt.
Reducing conditions: S dissolves as sulphide (S^{2-}) ions.
Oxidizing conditions: S dissolves as sulphate (SO_4^{2-}) ions.
Reduction of p_{O2} above a melt will cause a reduction in S solubility and bubbles will form.
Sulphate solubility decreases with increasing temperature, but sulphide solubility increases.

Oxygen: changes in oxidation state of polyvalent ions can change oxygen from chemically bound to physically dissolved molecules e.g.

$$4Fe^{3+} + 2O^{2-} \rightarrow 4Fe^{2+} + \uparrow O_2$$

Solubility of O_2 molecules is lower then that of O^{2-} ions so oxygen bubbles form.

Reboil: the formation of bubbles in previously bubble-free glasses or melts.
Occurs when a solid glass is reheated or a glass melt is heated to a higher temperature.
Gases which decrease in solubility with temperature cause reboil e.g. SO_3 solubility in soda-lime-silicate melts decreases by three orders of magnitude between 1100 - 1400°C.

Removal of bubbles by Buoyancy Effects

Bubbles can be removed from the melt by: rising to the surface and bursting
dissolving into the melt.

Stokes' law for a solid sphere in a liquid of different density.

$$V_S = \frac{2g\Delta\rho r^2}{9\eta}$$

V_s = velocity of solid sphere
g = gravitational acceleration
$\Delta\rho$ = difference in density between sphere and liquid
r = radius of sphere
η = viscosity of liquid

For a gas bubble in a viscous liquid: $V_b = \frac{3}{2} V_S = \frac{g\Delta\rho r^2}{3\eta}$ V_b = rate of rise of bubble

In practice, $V_b \rightarrow V_s$ as bubble size decreases i.e. small bubbles rise more slowly.

Bubbles rise more quickly in a fluid melt.
Bubbles rise more quickly in a dense melt.
Large bubbles rise more quickly than small ones.

Bubble removal can be speeded up by stirring the melt:
mechanical stirring
design of glass tank floor to produce upward currents
localized heating
gas bubbling from bottom of melt.

Fining Agents

- Fining agents: minor batch components which remove bubbles by chemical means.
- Release large amounts of gas which form large bubbles.
- These bubbles rise to the melt surface, dragging smaller bubbles along with them.
- Some fining agents cause O_2 in bubbles to dissolve into the melt, reducing bubble size.
- If the bubble becomes small enough, surface energy will cause it to disappear.

- As_2O_3 and Sb_2O_3 are the most efficient fining agents.
- 0.1 - 1 wt % is added to the batch, usually combined with alkali nitrates.
- A_s2O_3 reacts with alkali and alkaline earth oxides to form arsenates (AsO_4^{3-}) which are less volatile than As_2O_3.

During batch melting, the following reactions happen e.g. for As_2O_3 and KNO_3:

$$4KNO_3 + 2As_2O_3 \rightarrow 2K_2O + 2As_2O_5 + \uparrow 4NO + \uparrow O_2$$

NO and O_2 form large bubbles which stir the batch and rise to the surface, dragging smaller bubbles with them.

After the batch-free time, the melt is heated to a higher temperature. At higher temperatures, the pentoxides decompose into trioxides e.g.

$$As_2O_5 \rightarrow As_2O_3 + \uparrow O_2$$

The O_2 formed can rise to the surface or diffuse into nearby bubbles, increasing their size.

Lowering the temperature will shift this reaction backwards, absorbing dissolved O_2 from the melt. This causes O_2 in nearby bubbles to dissolve into the melt, reducing the bubble size.

$$P = \frac{2\gamma}{r}$$

P = gas pressure inside bubble
γ = liquid / vapour interfacial energy
r = radius of bubble

When $r < 0.1$ mm, P is high enough to accelerate O_2 diffusion from bubble to melt, and it disappears.

Other fining agents

As_2O_3 and Sb_2O_3 are both toxic, so other fining agents are often used.

Sodium sulfate: Sulfates dissolve easily in alkali-rich melts.
As the batch melts and SiO_2 concentration in the melt increases, sulfate solubility decreases:

$$Na_2SO_4 + nSiO_2 \rightarrow Na_2O{-}nSiO_2 + SO_3 \quad \Longrightarrow \quad 2SO_3 \rightarrow 2SO_2 + O_2$$

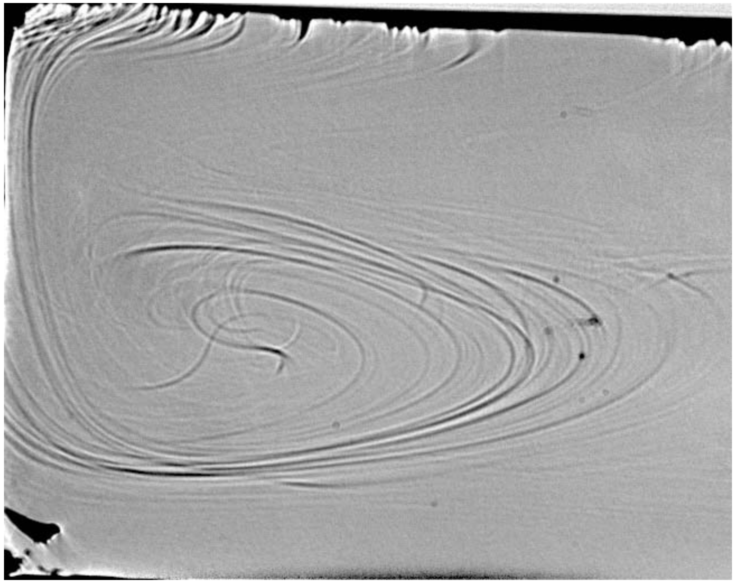
SO_2 diffuses into nearby bubbles. O_2 dissolves or diffuses into bubbles.
Bubbles then rise to surface.
Lowering the melt temperature causes SO_2 to redissolve in the melt, causing bubbles to shrink.

Halides: Halides lower melt viscosity, causing bubbles to rise faster.

Polyvalent oxides: e.g. cerium

$$4CeO_2 \rightarrow 2Ce_2O_3 + \uparrow O_2$$

Homogenizing of Melts



The melt just after batch decomposition is very *heterogeneous* i.e. batch composition varies with position.

Gr heterogenēs < hetero-, other + genos, a race, kind

Extra time is needed to improve homogeneity by diffusion.

Stones: particles of unmelted batch, bits of refractory.
Striae: 2D layers with different composition.
Cord: 1D lines with different composition

Cause a "wavy" appearance in the glass due to local changes in refractive index.
Can be examined visually using a zebra board or shadow graph.

Causes: poor batch mixing
reaction with refractories
volatilization

Decreasing the grain size of batch components, good batch mixing and mechanical stirring of the melt can improve homogeneity.

Glass Melting Furnaces

Three groups:

Pot furnaces: glass is melted in ceramic pots. Periodic operation (24-hour working cycle). Used for melting special glasses in small quantities.

Continuous tank furnaces: batch is continuously fed into one end and glass is continuously drawn out of the other. Highly automated. Economical for high tonnage production.

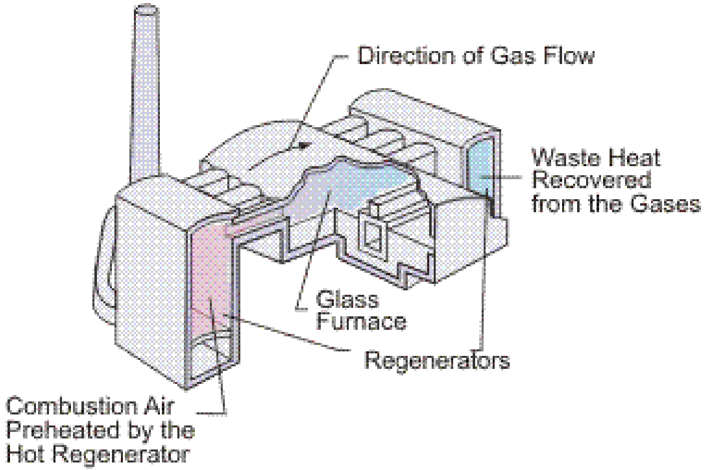
Electric furnaces: used in special applications.

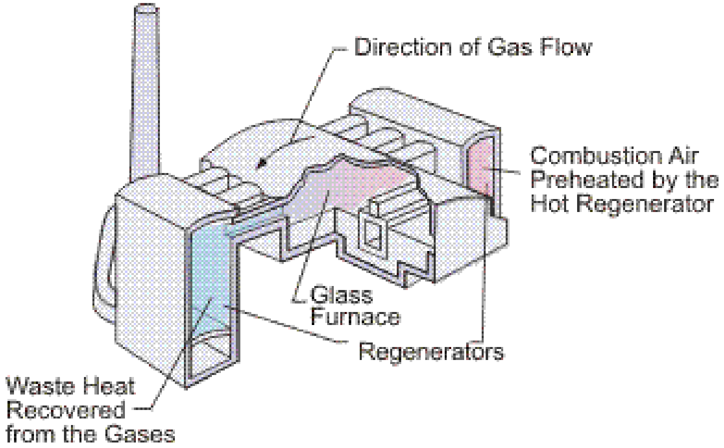
Heated by: natural gas
fuel oil
electrically heated
combination of the above

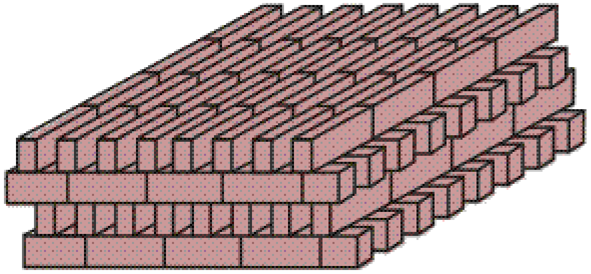
http://www.sorg.de/pdf/glas_melting.pdf

Regenerators

- Recovers heat from exhaust gases.
- Consists of two chambers containing ceramic bricks.
- Exhaust gases are passed through one chamber.
- Bricks heat up.
- After ~30 mins, direction of gas flow is reversed.
- Air for combustion is preheated by passing through the hot chamber.
- High alumina refractory bricks are used (must withstand corrosion from Na_2O, $NaSO_4$ and SiO_2 vapours).







Pot furnaces

- Low melting output and heat utilization.
- Used for small quantities of glass (coloured, art glass or optical)
- Furnace space holds 4 - 12 pots of height 50 - 80 cm.
- Heated by flame passing horizontally between side ports.
- Batch is loaded into the pot 2 or 3 times.
- Temperature is incerased for refining / homogenization.
- Homogenization is assisted by mechanical stirring or blowing air into the glass through a cooled metal tube.
- Melted glass is removed manually through holes in the furnace side wall above each pot.
- Thermal efficiency is very low, < 10 %.
- Single pot furnaces are used for melting optical glasses.

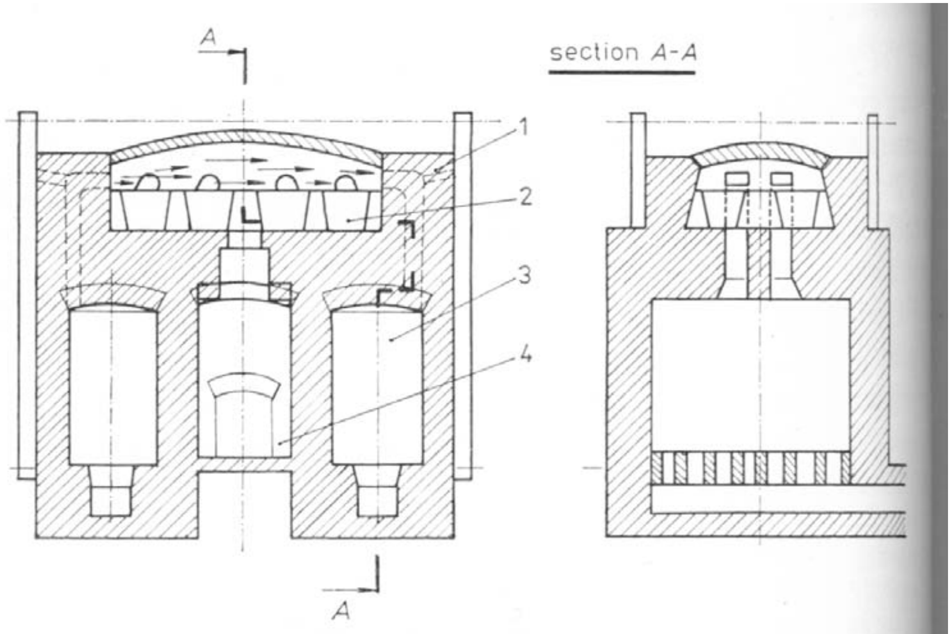


FIG. 95. Top-flame pot furnace. (1) port nozzle for town gas, (2) pot, (3) regener
chamber, (4) running-out pit

Continuous tank furnaces

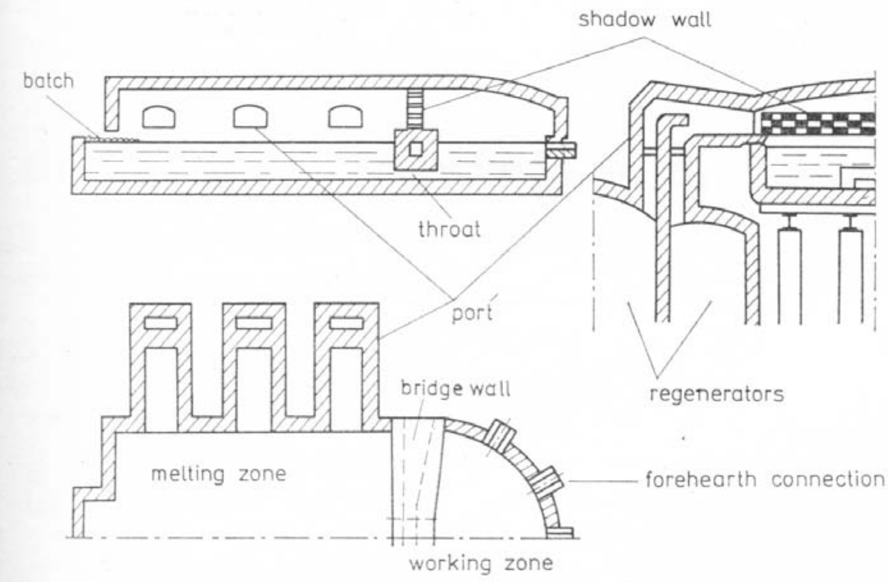


FIG. 96. A cross-fired tank furnace for container glass production (after Günther, 1954, modified).

- Batch is continuously fed in at the left.
- Glass is continuously drawn out at the right.
- Batch and melt are heated by combusting gas above the melt surface.
- The melting and refining zones are combined in a single unit called the melting end or melter.
- A thermal barrier (temperature maximum) prevents unmelted batch from passing into the refining zone.
- The melting end is separated from the working end by a barrier.
- The molten glass passes below the barrier, which removes surface impurities.
- At the working end, the melt is cooled until its viscosity is suitable for forming.
- For soda-lime-silica glassses, the atmosphere above the melting area should be reducing and the atmosphere above the refining and working areas oxidizing.
- This can be controlled by adjusting the fuel / air ratio.
- Container glass tank furnaces: melting area 20 - 100 m^2, 50-300 tons of glass per day.
- Sheet glass tank furnaces: melting area up to 400 m^2, 50-700 tons of glass per day.
- Technical glass tank furnaces e.g. optical have smaller melting area and output.

Electric boosting

- Thermal efficiency of glass furnaces is low (20 - 35 %)
- The melt at the bottom of the tank is difficult to heat.
- Molybdenum electrodes can be installed in the tank to pass AC electric current directly into the melt.
- The melt gains additional heating from Joule heating.
- Electrodes can be placed in the side walls or bottom of the tank.
- Melting capacity can be increased.
- Heat can be supplied to parts of the furnace that are difficult to heat.
- Convection in the melt is increased, which helps homogenisation.

http://www.sorg.de/pdf/electric_boosting.pdf

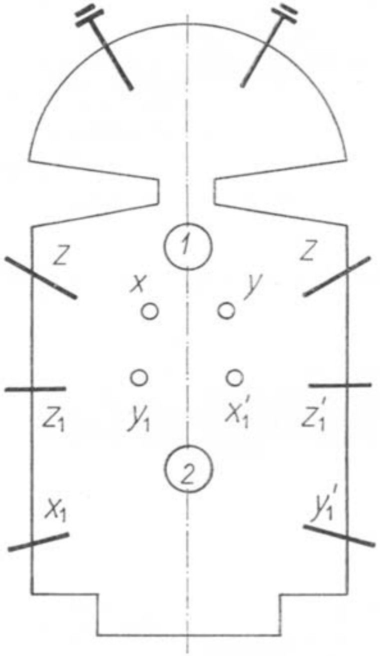


FIG. 100. Container glass tank
electric boosting using six horizontal
four vertical electrodes (X, Y, Z
connection of the source phases, 1
2 — independent heating circuits).

Electric furnaces

- Electric continuous melting furnaces have outputs from several tons - 120 tons per day.
- An example is the Gell furnace used for melting borosilicate glasses.
- Mo plate electrodes (5) are placed along the entire length of the tank walls (1).
- The glass melts below a layer of batch which reduces heat losses and volatilisation of volatile components.
- Refined melt flows through a submerged throat (2) into the working chamber (3, 4).

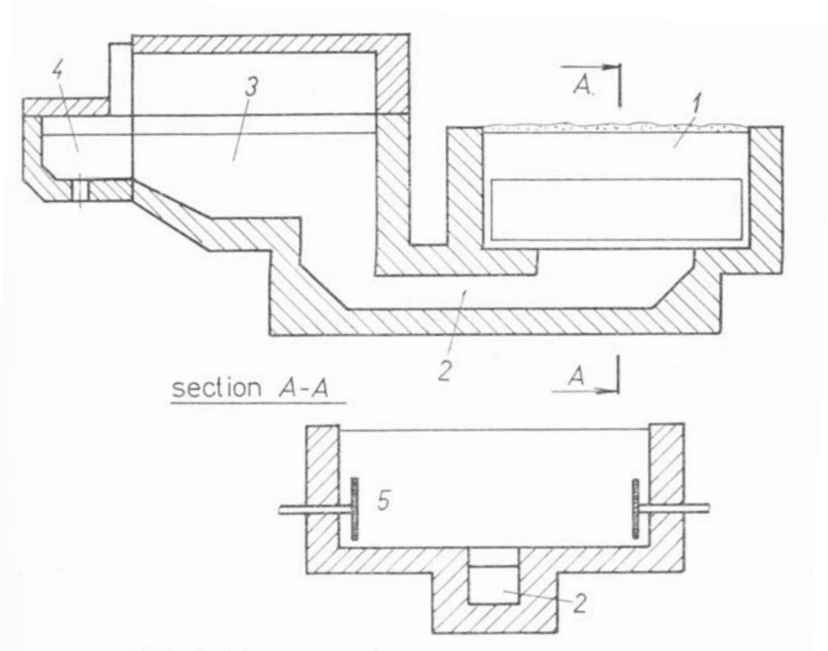


FIG. 101. Gell's electric melting furnace.

Electric furnaces have the following advantages:

1. suppressed volatilisation of toxic materials e.g. PbO
2. savings in raw materials
3. high production per unit melting area of furnace
4. high thermal efficiency (60 - 80 %)

Mo electrodes are unsuitable if they are corroded by the melt e.g. optical glasses, lead glasses
SnO_2 electrodes are suitable for melting lead glasses.

Refractories

- Refractories must: withstand high temperatures;
  remain inert in severe environments (high temp, corrosive atmosphere or liquids)
  provide thermal insulation
- Several types: Fireclay, Silica, Basic and Special Refractories.
- Porosity: As porosity ↑, strength and corrosion resistance ↓, thermal insulation ability and thermal shock resistance ↑.

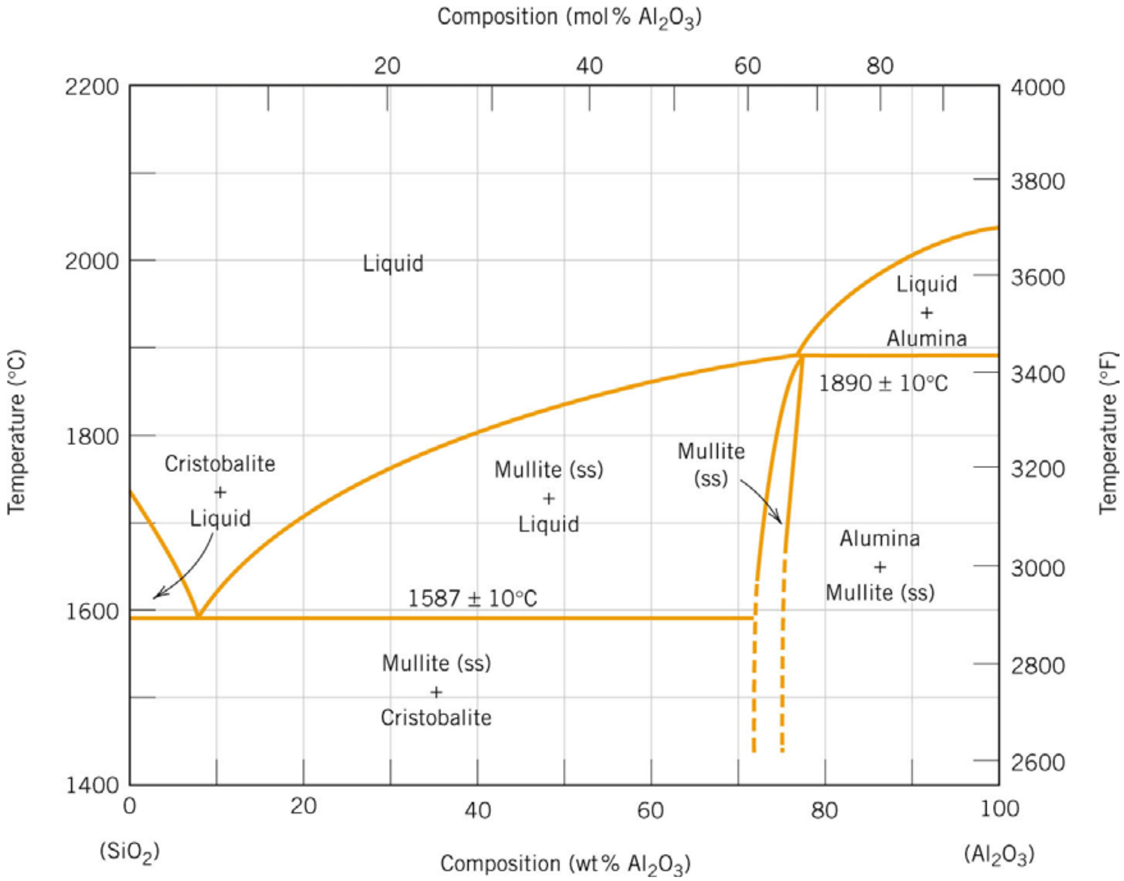
Fireclay (Al_2O_3 – SiO_2 mixtures, 25-45 wt % Al_2O_3): tank bottom, side walls and regenerators.

Silica: crown (roof)

Al_2O_3-ZrO_2-SiO_2 fusion cast refractories: Melt line, throats, ports, electrode blocks, side walls at the melting end of high-temp furnaces.

Fireclay Refractories.

- $Al_2O_3 – SiO_2$ mixtures (25-45 wt % Al_2O_3).
- Max. temp without liquid phase = 1587°C.
- During use, formation of a small amount of liquid phase may be allowable.
- ↑ Al_2O_3 content reduces amount of liquid phase formed and increases max service temp.
- Uses: furnace construction, thermal insulation of structural members.
- Now replaced by fusion cast AZS refractories.



Silica Refractories

- Uses: roofs of steel- and glass- making furnaces.
- Max. service temp: 1650°C.
- Small amount of liquid phase may be present.
- Al_2O_3 content must be kept low (0.2 – 1 wt %) due to eutectic at 7.7 wt % Al_2O_3.
- Silica refractories are resistant to silica rich slags or liquids (acid slags).

Fusion cast Refractories

- Refractory composition (Al_2O_3, 1 - 1.7 wt % Na_2O, 11-15 wt % SiO_2 and 34-41 wt. % ZrO_2) is melted at 1900 - 2500°C in an electric arc furnace, poured into a mold and cooled slowly.
- Consists of Al_2O_3 and ZrO_2 crystals in a glass matrix.
- Highly corrosion-resistant, high density, low porosity, good mechanical properties.
- Al_2O_3, Al_2O_3-ZrO_2 and > 90 wt % ZrO_2 compositions also used.
- More recently, reduction in production costs has led to their use in tank side walls and bottoms.

RHI AG

Viscosity

Viscosity is a measure of the resistance of a liquid to shear deformation.

The flow behaviour of glasses is determined by viscosity.

$$\boxed{\tau = \frac{F}{A} = \eta\frac{d\nu}{dx}}$$

$$\boxed{\eta = \frac{Fd}{A\nu}}$$

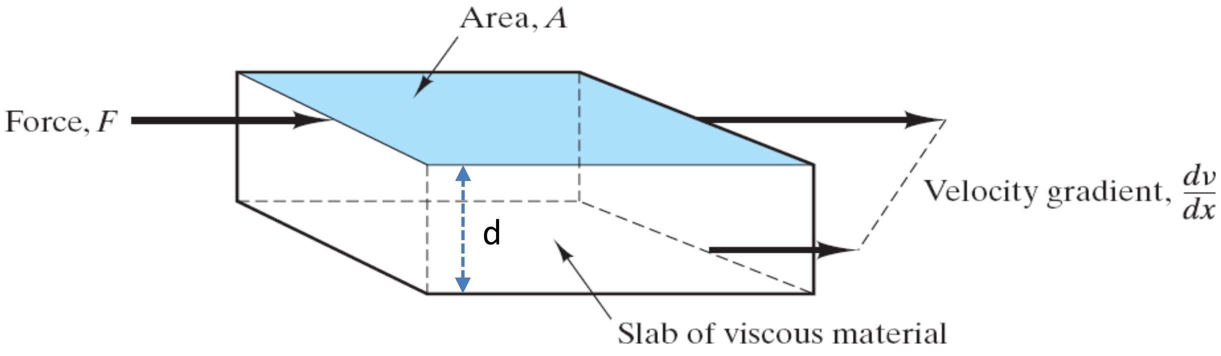


Figure 6-41 *Illustration of terms used to define viscosity, η, in Equation 6.19.*

- If η is independent of F, liquid is *Newtonian*.
- At high τ, many glass melts show *shear thinning* - η decreases with τ.
- Original unit of η is the poise (P) - 1.00 $g.cm^{-1}.s^{-1}$ (cgs system)
- Now measured in Pa s - 1.00 $kg.m^{-1}.s^{-1}$
- 1 Pas = 10 P

τ = applied shear stress
F = shearing force
A = area
d = thickness
η = viscosity (poise, P, = 1 g/(cm.s) = 0.1 Pa.s)
$d\nu/dx$ = velocity gradient between top and bottom of material.
ν = relative velocity of top and bottom planes of material

Below T_g, material deforms elastically.
Above T_g, material deforms by viscous flow.

Important Temperatures

- Melting range: η = 50-500 P – glass is fluid enough to be considered a liquid.
- Working range: $\eta = 10^4 – 10^8$ P – products can be shaped.
- Softening point: $\eta = 10^{7.6}$ P – lower temperature end of working range.
- Annealing range: $\eta = 10_{12.5} – 10_{13.5}$ P – residual stresses can be relieved.
- Annealing point: $\eta = 10^{13.4}$ P – internal stresses can be removed in ~ 15 mins. $T_g \approx$ annealing point.
- Strain point: $\eta = 3\times10^{14}$ P. Below this temp, fracture occurs before onset of plastic deformation.

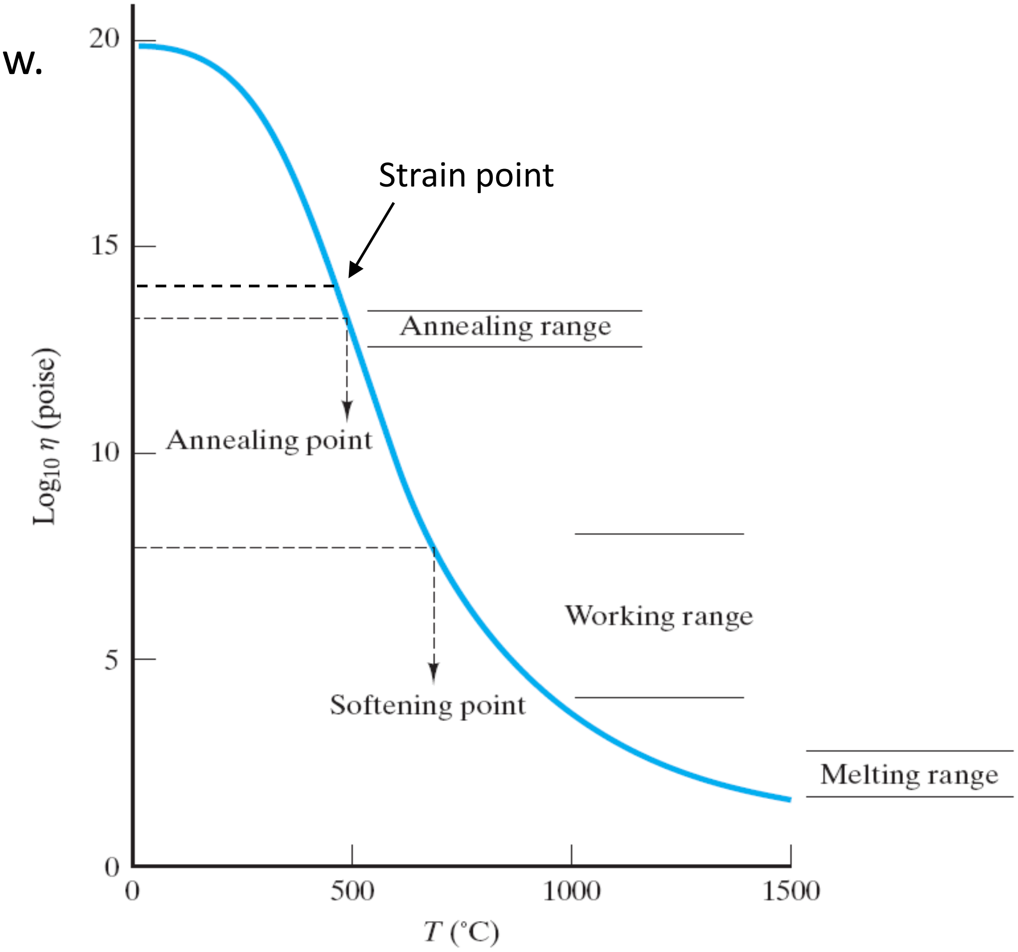
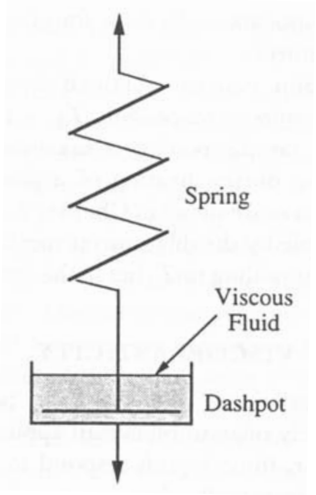


Figure 6-42 *Viscosity of a typical soda–lime–silica glass from room temperature to 1500°C. Above the glass transition temperature (~ 450°C in this case), the viscosity decreases in the Arrhenius fashion (see Equation 6.20)*

- Formation of a glass object requires careful control of viscosity.
- A viscous blob of liquid (gob) must be shaped into an object e.g. a bottle.
- The liquid must be fluid enough to flow under applied stress, but viscous enough to keep its shape after forming.
- The gob is delivered to the forming machine at a viscosity of 10^3 Pa s - the *working point*.
- Once the object has formed, it must be supported until its viscosity increases to $10^{6.6}$ Pa s - the *softening point*. At this point, the object will not deform under its own weight.
- The temperature range between the working and softening points is called the *working range*.
- Melts with a large working range are called long glasses. Melts with a small working range are called *short glasses*.
- After forming, the object is cooled. Internal stresses form during cooling and must be removed by *annealing*. The *annealing point* (10^{12} or $10^{12.4}$ Pa s) is the temperature at which stresses can be substantially reduced in a few minutes.
- The strain point ($10^{13.5}$ Pa s) is the temperature at which stresses can be substantially reduced in a few hours.
- *Glass transformation temperature T_g* - for common glasses has a corresponding viscosity of $10^{11.3}$ Pa s.

Viscoelasticity

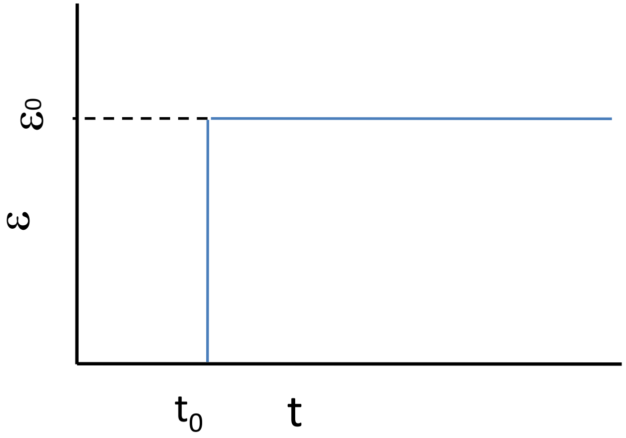
At intermediate η, the glass melt is ***viscoelastic*** – combined elastic and viscous behaviour.



- Viscoeleastic behaviour can occur in the η range 10^{13} - 10^8 Pa s i.e. in the glass transformation range.
- The *Maxwell model* is the basic model for viscoelasticity.
- The sample is represented by an elastic element (spring) connected in series with a viscous element (a piston in a cylinder filled with viscous liquid - called a *dashpot*).

- Apply a force to the Maxwell element - the element will respond i.e. the bottom of the element (point A) will move to a new position (point B).
- If the liquid has infinite η, the deformation is due to the spring stretching - the response is perfectly elastic. If the force is removed, the bottom of the element will return to point A.
- If the liquid has zero η, the deformation is due to movement of the dashpot only - the response is perfectly plastic. If the force is removed, the bottom of the element will remain at point B.
- If the liquid has intermediate η, the initial response is perfectly elastic - the spring stretches. Then, liquid in the dashpot will flow and the piston will move upwards in the dashpot. The spring will go back to its original length. The strain in the spring is relieved and the force needed to maintain the bottom of the element at point B will decrease to zero. Deformation of the element is then permanent.

Calculating stress as a function of time:

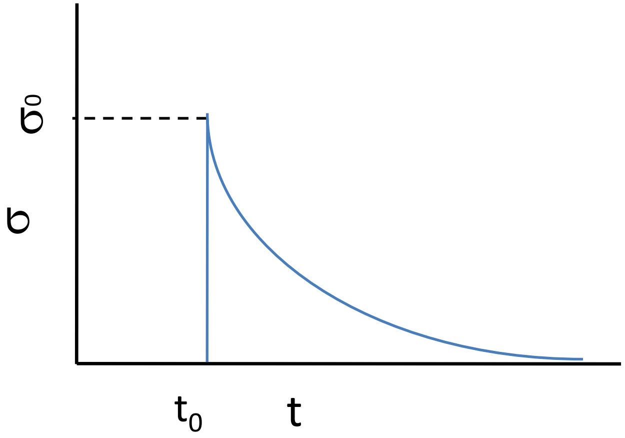


$$\sigma_t = \sigma_0 \, exp\left(-\frac{Gt}{\eta}\right)$$

σ_t = stress at time t
σ_0 = stress at time zero
G = shear modulus
η = viscosity

The ratio η/G is called the *relaxation time* τ. It is the time needed for the stress to decay to 1/e (0.367) of σ_0.

We can rewrite the equation as:



$$\sigma_t = \sigma_0 \, exp\left(-\frac{t}{\tau}\right)$$

Assuming G ≈ 10^{11} Nm^{-2}, the value of τ at $\eta = 10^{12}$ Pa s is 10 seconds. Relaxation of ~ 95% of initial stress will happen in 3τ or 30 seconds.

The Maxwell model is too simple - better models include Voigt-Kelvin elements (a spring and dashpot in parallel) or a Burger element (a Maxwell element in series with a Voigt-Kelvin element).

Temperature Dependence of Viscosity

Arrhenian behaviour

Observed within the glass transformation range (10^{13} - 10^{9} Pa s) and at high temperatures.

$$\eta = \eta_0 \, exp\left(\frac{\Delta H_\eta}{RT}\right)$$

η = viscosity
η_0 = constant
ΔH_η = activation energy for viscous flow
R = universal gas constant
T = absolute temperature

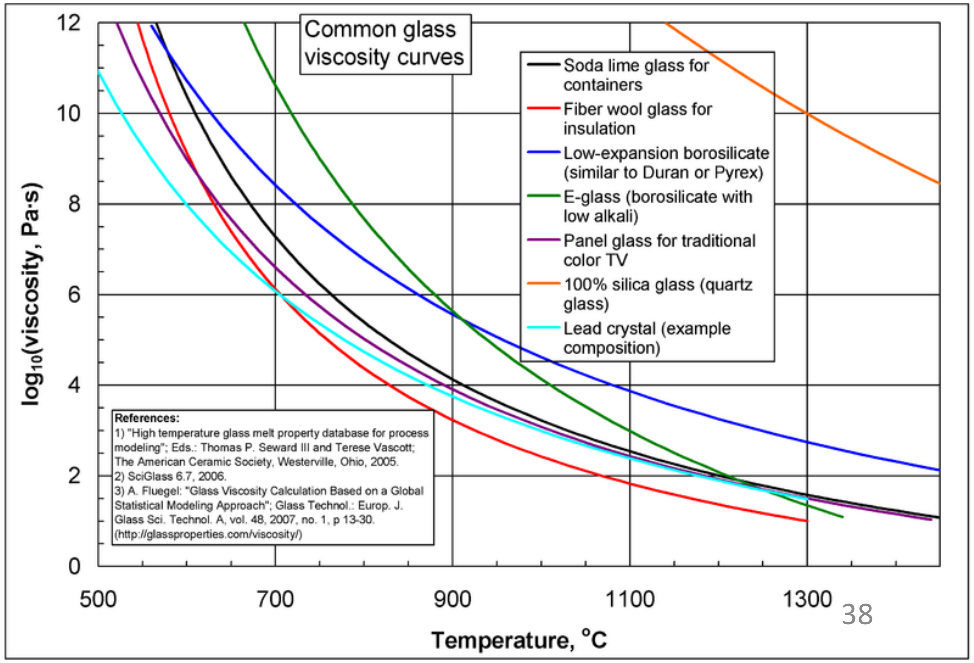
Note: ΔH_η in these two regions has different values. Between these regions, ΔH_η varies with T and the behaviour is non-Arrhenian.

Vogel-Fulcher-Tamman

$$\eta = \eta_0 \, exp\left(\frac{B}{T - T_0}\right)$$

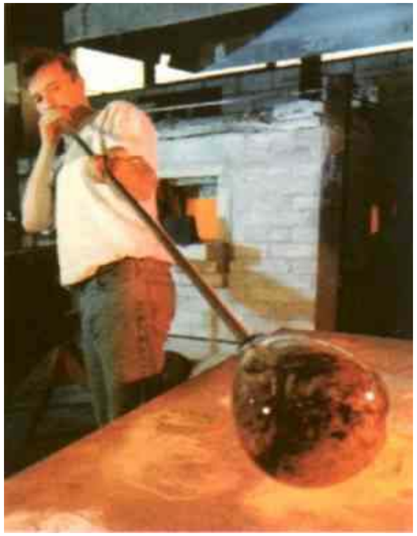
T_0 = fitting factor to account for variable ΔH_η
B = variable

Provides a good fit to viscosity data over the entire temp range but tends to overestimate viscosity at the lower end of the transformation region.



References:
1) "High temperature glass melt property database for process modeling"; Eds.: Thomas P. Seward III and Terese Vascott; The American Ceramic Society, Westerville, Ohio, 2005.
2) SciGlass 6.7, 2006.
3) A. Fluegel: "Glass Viscosity Calculation Based on a Global Statistical Modeling Approach"; Glass Technol.: Europ. J. Glass Sci. Technol. A, vol. 48, 2007, no. 1, p 13-30. (http://glassproperties.com/viscosity/)

Glass Forming



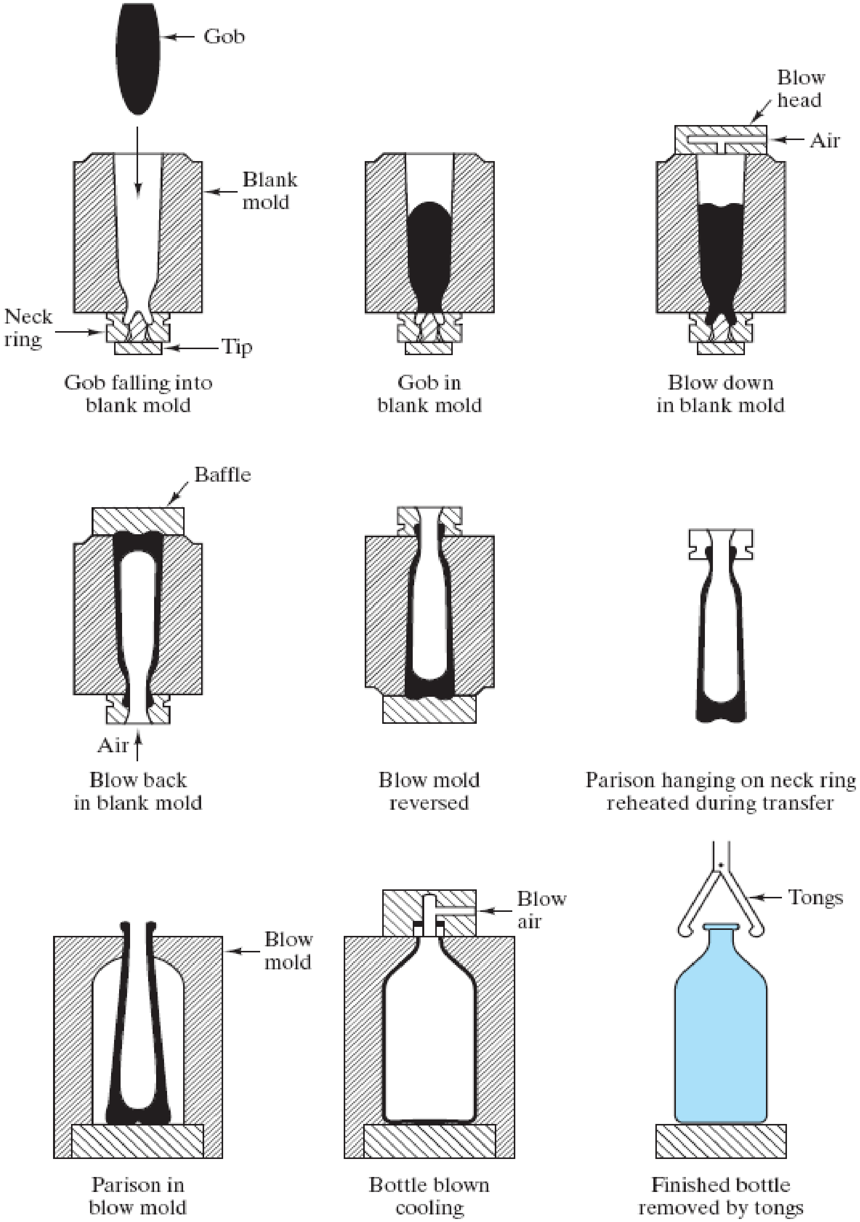
Classical forming methods - containers

- Originally *hand blown*.
- A blowpipe is dipped into the melt to gather a gob of glass.
- Air is blown through the pipe and the gob expands to form a hollow shell of glass.
- The glass can be shaped using wooden paddles.
- The gob can also be placed in a mold before blowing.
- Complicated shaped can be produced.
- Still used for studio glass (artistic glass).
- Most modern container glass is produced in mechanical blowing machines.

- A gob of molten glass is placed in a split mold, where it is blown into a approximate shape (*parison*).
- The parison is transferred to a blow mold, reheated and blown into final shape.
- For wide-mouthed containers, the parison is formed by pressing instead of blowing.
- After removal from the mold, the containers are annealed to remove thermal stresses.

Most container glasses are made of soda-lime-silica glass (73 wt % SiO_2, 11 wt % CaO, 14 wt % Na_2O and 2 wt % Al_2O_3).
Containers for chemicals or pharmaceuticals are made from borosilicate glasses.

http://www.recycleglass.co.nz/images/process-bb.swf



Gob falling into blank mold

Gob in blank mold

Blow down in blank mold

Blow back in blank mold

Blow mold reversed

Parison hanging on neck ring reheated during transfer

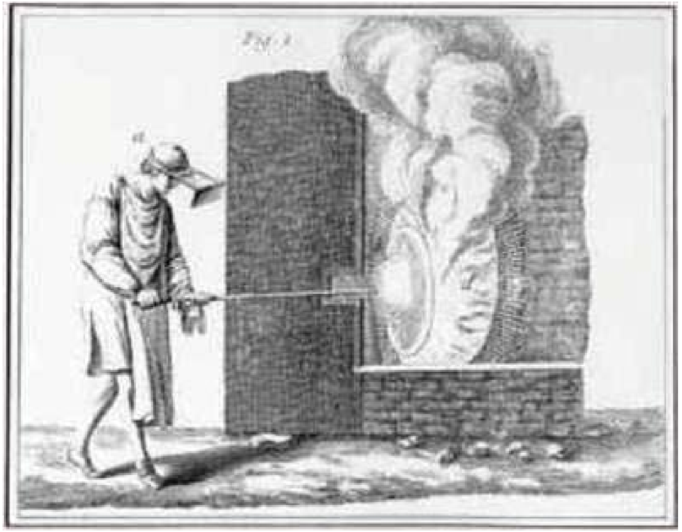
Parison in blow mold

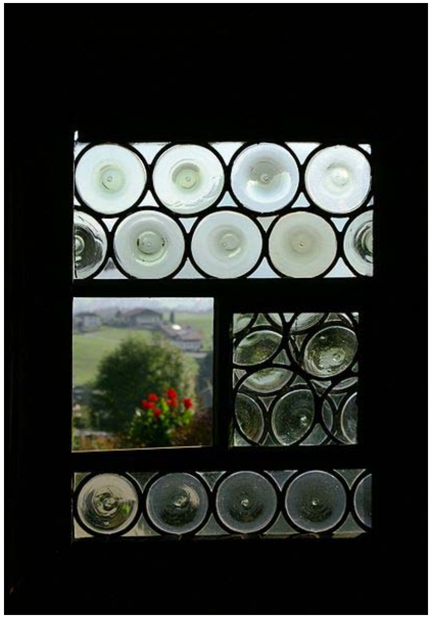
Bottle blown cooling

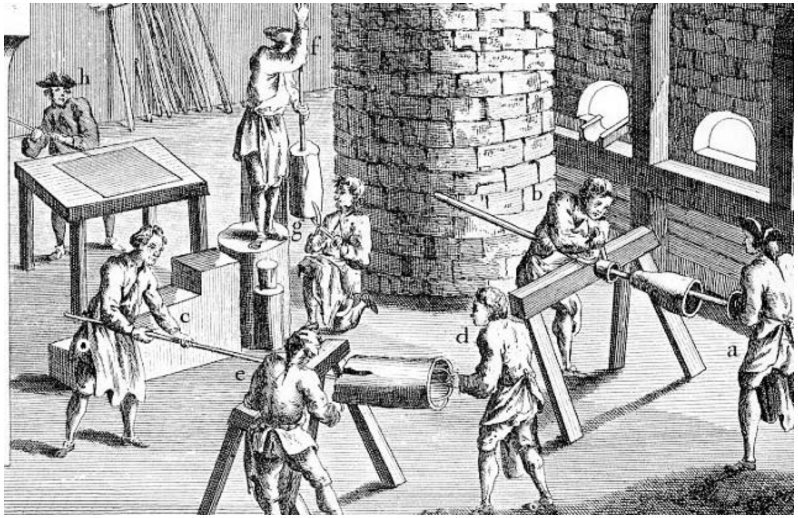
Finished bottle removed by tongs

Flat glass

- ***Crown method***: A gob was gathered on the end of a pipe and spun inside the furnace.
- Centrifugal force flattened the glass into a disc.
- Window panes were cut from the outer part of the disc.
- The outer edge of the disk is thinner than the center.
- The centre of the disc is used in decorative windows.
- ***Broad glass***: the gob is blown into a cylindrical shape.
- The cylinder is split parallel to its axis and flattened by reheating on a flat surface.
- Machine cylinder method: a large cylinder (12m high) is drawn vertically from the melt, annealed, cut into smaller cylinders (3m high), then split and flattened as before.







Sheet glass (Fourcault drawing)

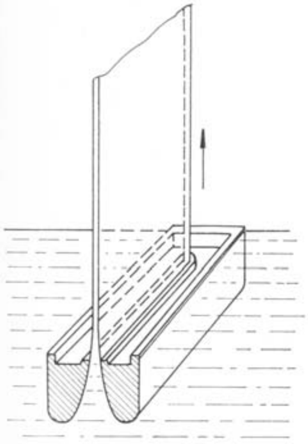


FIG. 105. Sheet glass drawing by means of the debiteuse.

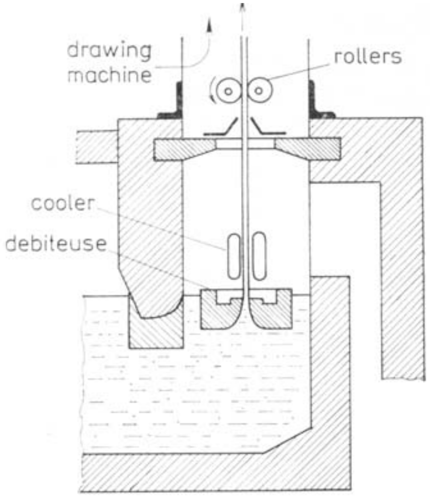


FIG. 106. Sectional view of the drawing compartment of the Fourcault drawing machine.

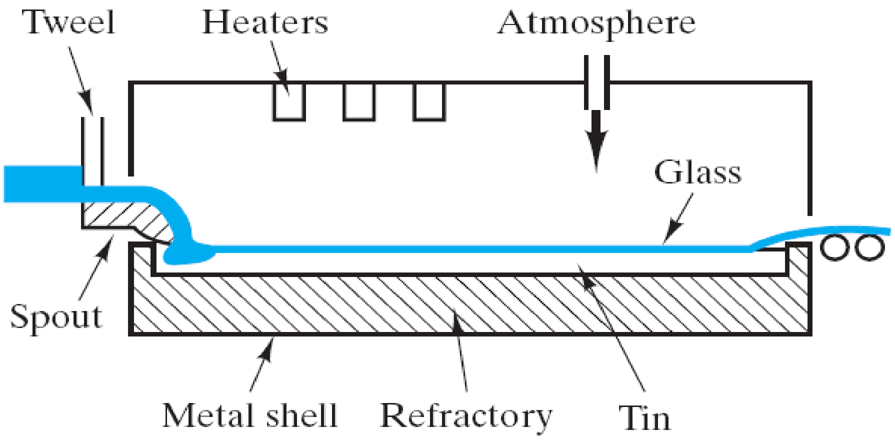
- A ribbon of glass is drawn vertically from the melt surface using a debiteuse made of fireclay.
- The debiteuse is boat-shaped with a longitudinal slot, and is pressed into the surface of the glass.
- The debituese keeps sheet width constant.
- Coolers ensure rapid solidification of the melt.
- The solid glass ribbon is drawn up by rollers, cooled and cut into sheets.
- Average sheet width is 2 m, thickness can be from 0.8 - 10 mm.
- Optical defects can by caused by the debiteuse slot surfaces.

Plate glass

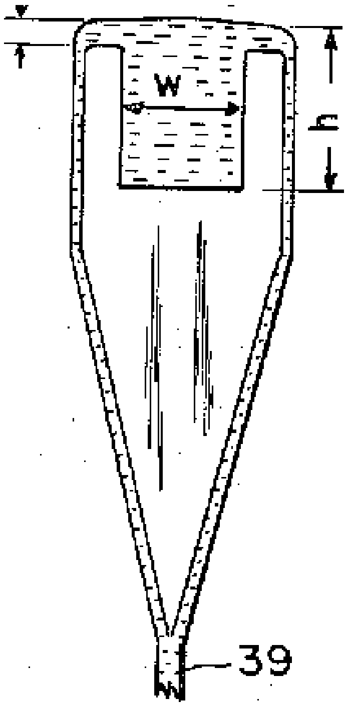
- Molten glass is cast on a metal table and rolled into a sheet.
- Can also be continuously rolled between water-cooled rollers.
- The glass is then ground and polished to an optical finish.
- Good optical properties but expensive.

Float glass

- Molten glass is floated on a bath of molten tin at high temperature.
- The glass spreads across the surface of the tin to form a flat sheet. Thickness is controlled by surface tension.
- The furnace atmosphere must be reducing to avoid oxidation of the tin.
- Produces glass with an excellent surface finish,
- The final glass has a considerable concentration of tin in the surface which was in contact with the tin.



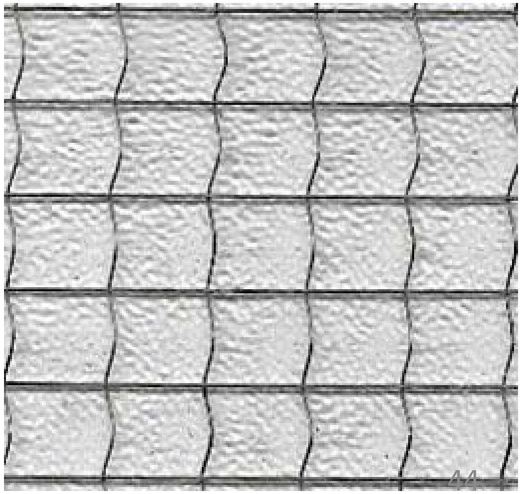
Fusion (downdraw) process



- Melt flows into shallow trough.
- Melt overfills the trough and flows over each side.
- The two meltstreams rejoin below the trough to form a single sheet of glass.
- Sheet thickness is controlled by pull rate.
- Surface finish is similar to the float process.
- A wide variety of glass compositions can be drawn (float glass process is restricted to soda-lime-silica glasses).

Wire mesh glass: mesh is placed into the molten glass which is then passed through rollers.

Microsheet glass: the melt is drawn through a slit in a platinum plate.
Glass thickness is controlled by pull rate.
Very thin glass can be produced (≤ 150 μm)
Used for microscope cover slips.



Glass Fibres

Uses: thermal insulation
fire resistant textiles
reinforcing fibres for composites

Chopped (discontinuous fibres)

- A thin stream of molten glass falls into a spinning cylinder which has a large number of holes in its surface.
- Centrifugal force pushes (extrudes) the glass through these holes into a high velocity gas stream.
- This gas stream breaks the fibres into small lengths.
- A chemical binder (sizing) is sprayed onto the fibres to hold them together.
- The sizing is a thermosetting resin.
- The fibres fall onto a conveyer belt and form a mat.
- This mat is then passed through an oven to cure (set) the binder.
- The mat can then be cut into the desired shapes.

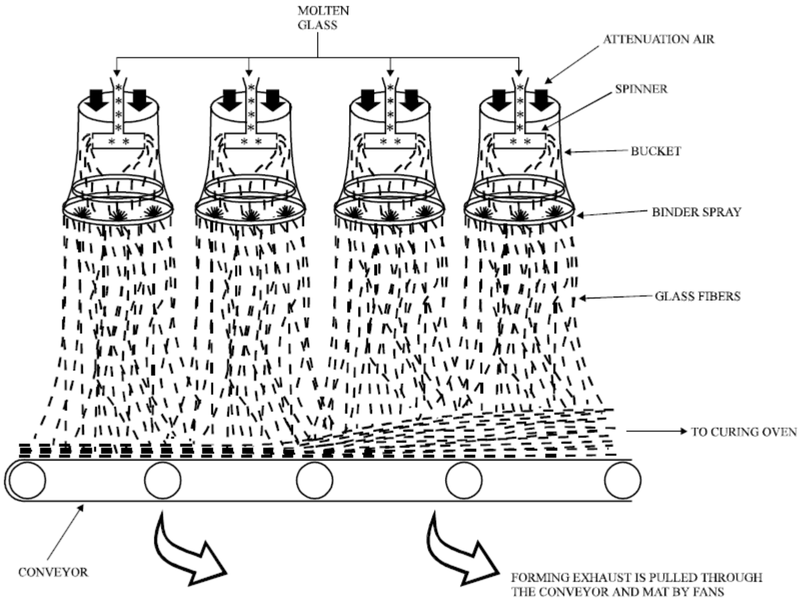


Figure 11.13-2. A typical spin process.

Continuous fibres

- Most continuous fibres are formed from E-glass, alkali earth alumino-borosilicate compositions.
- Produced directly from the melt or from remelted glass marbles.
- Melt is extruded through orifices (holes 0.8 - 3mm diameter) in a Pt-Rh alloy *bushing*.
- The glass filaments are coated with sizing then gathered into a single strand.

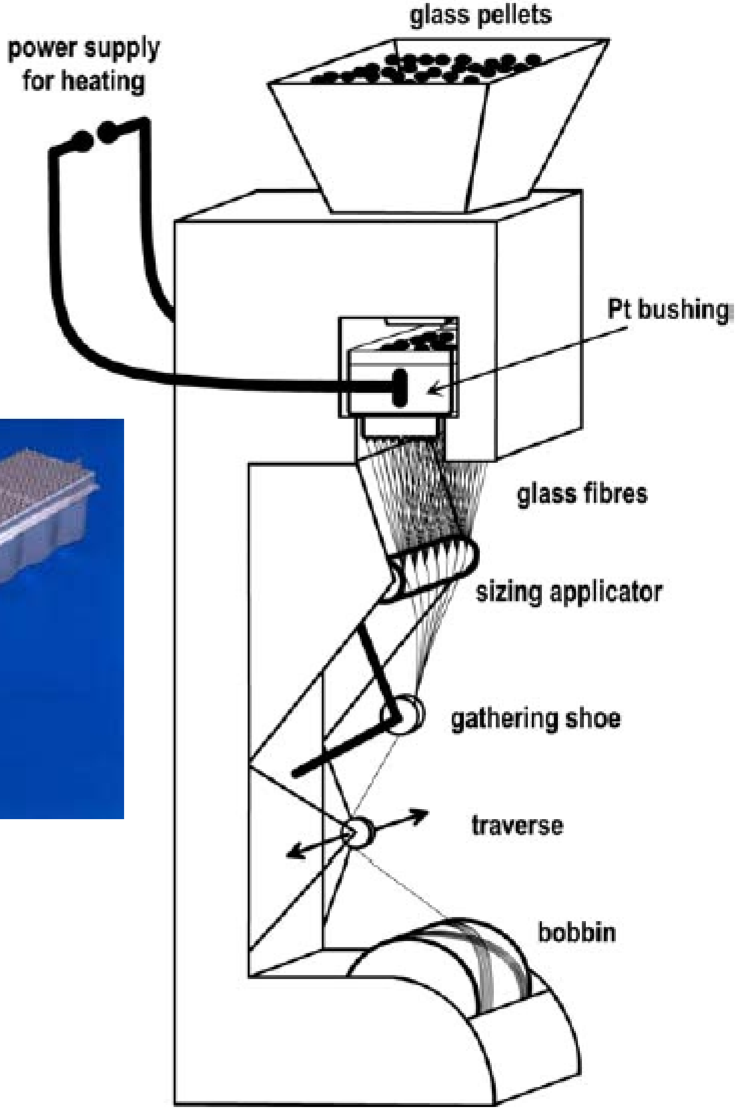


Figure 1. Pt-bushing for production of continuous glass fibres.

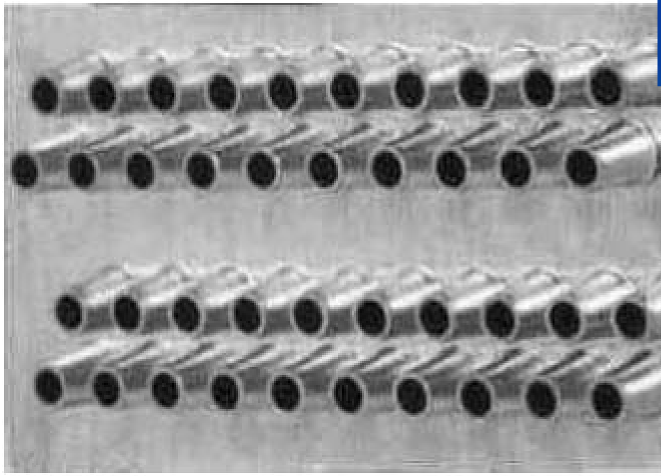


Figure 2. Four tip rows pressed in the base-plate of Pt-bushing for production of continuous glass fibres.