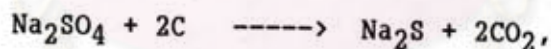


Chapter II

Theoretical Part

2.1 Thermodynamics of batch melting

Liquid phase formation during batch melting is a key event. Therefore, a detailed literature study on the thermodynamics of primary liquid phase formation was performed. Typical batches of the soda lime silicate glasses usually contain low-liquidus compounds like Na_2CO_3 , Na_2SO_4 , and NaNO_3 . Beside this, Na_2S has to be taken into account as an intermediate low-liquidus product of the sulfate-coal reaction



2.1.1 Primary melt formation

Solid state reactions are an essential part of batch melting, yet the predominant influence on the reaction rate is exerted by the first substantial amount of liquid phase generated in the system. The properties of this primary melt, i.e., its viscosity, interfacial tension, and affinity towards residual solids determine the further course of batch melting.

2.1.2 Direct melting

The most straight-forward way of primary liquid phase formation is direct (physical) melting. For typical mass glass batches, this refers to Na_2CO_3 , Na_2SO_4 , and NaNO_3 . The phase diagram in figure 2.1 shows the effect of mutual mixing. The melts have low viscosities typical of ionic melts (estimates by the Stokes-Einstein equation range from 0.1 to 1 dPas), allowing them to rapidly fill the voids in the batch. An important case of direct melting is the melting of cullet. It does not occur at a distinct temperature and does not involve a melting enthalpy, but proceeds as a sub-liquidus softening. Viscosities $< 10^5$ dPas are typically not found below 900 °C.

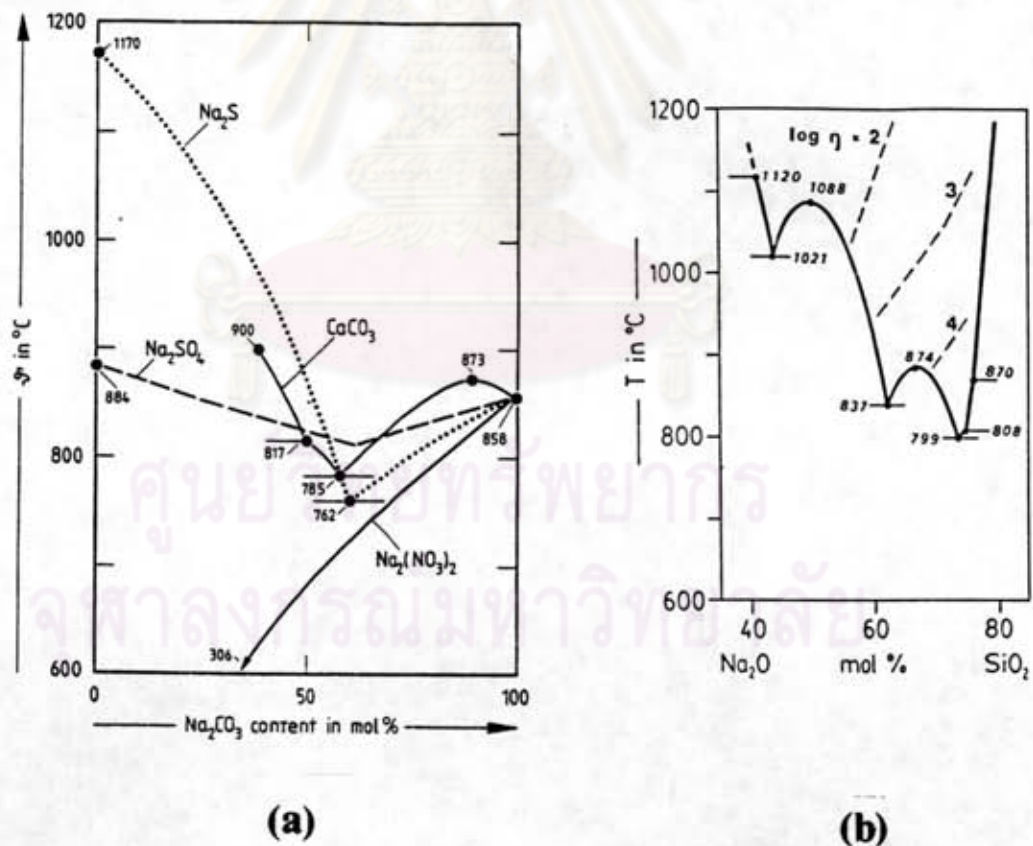


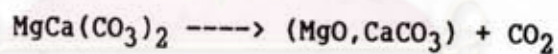
Figure 2.1. Liquidus curves of the binary systems of Na_2CO_3 with Na_2S , Na_2SO_4 , CaCO_3 , or NaNO_3 (a), and of the sodium silicate system (b).

2.1.3 Sulfate reduction

Sulfate reduction occurs under distinctly reducing conditions yielding Na_2S (besides other sodium-sulfur compounds) as an intermediate product. Na_2S forms a low-temperature eutectic with Na_2CO_3 at $762\text{ }^\circ\text{C}$, thus acting as a melt accelerator. The temperature is among the lowest liquids temperatures possibly established in mass glass batches.

2.1.4 Reactive carbonate melting

Carbonates typically present in mass glass batches are soda ash, limestone, and dolomite. Upon heating-up, limestone decomposes to CaO and CO_2 at 900 and $800\text{ }^\circ\text{C}$ in atmospheres with 1 and 0.2 bar CO_2 partial pressure, respectively. Dolomite decomposes in two steps. The first step

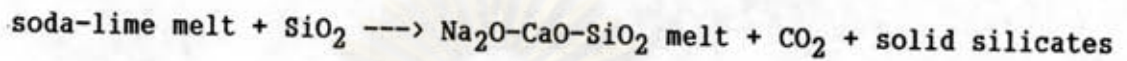


is completed at 680°C , the second one is identical to the limestone decomposition. None of these reactions generates primary melt. However, Na_2CO_3 and CaCO_3 form a low-temperature eutectic at $785\text{ }^\circ\text{C}$ located between the reaction point of $\text{Na}_2\text{Ca}(\text{CO}_3)_2$ ("double salt") at $817\text{ }^\circ\text{C}$ and pure Na_2CO_3 . The corresponding soda-lime melt has a low viscosity typical of ionic melts.

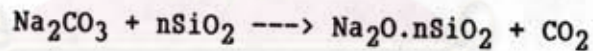


2.1.5 Reactive silicate melting

The direct reaction between SiO_2 and CaCO_3 is of little significance for the overall reaction rate and shall not be discussed here. However, with a soda-lime melt already present, a reaction of the type

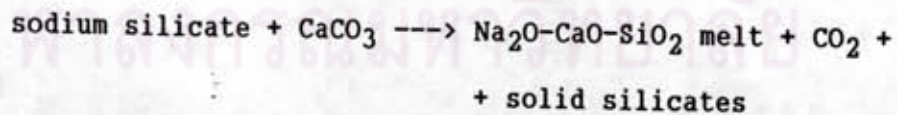


takes place. It accounts, under certain boundary conditions, for a sudden and substantial increase of the overall reaction rate in a melting batch at 785°C ; this coincides with the soda-lime eutectic. Yet another route towards the ternary silicates is possible: This route starts with a reaction between SiO_2 and Na_2CO_3 , typically occurring as a solid state reaction already and proceeds according to the pattern (see also figure 2.1)



with $n = 1/2, 1, 2, 3$.

By a further reaction of the type



the ternary melts with their much lower liquidus temperatures are accessible. In the presence of feldspar other reactions may predominate.

Finally, the MgO generated during dolomite decay is reported to form a $\text{Na}_2\text{O-MgO-SiO}_2$ eutectic at 700°C .

2.1.6 Primary melt formation and electrical conductivity

Electrical conductivity is chosen as the local indicator of the first occurrence of liquid phase. This approach has been suggested and used before. Actually, however, the relation between liquid phase formation and electrical conductivity in a multiphase system is not unambiguous and requires some discussion beforehand. In a continuous one-phase (solid or liquid) electrolyte system, electrical conductivity is directly correlated to ionic mobility (ionic diffusion). As visualized from a simple hopping mechanism, ionic mobility depends on the free space available for the ionic motion (defect concentration, free volume) and on the activation energy of the motion itself. As the Na^+ ion is the predominant charge carrier in commercial batch compositions, the behavior of sodium salts in general is discussed. In the solid state, ionic mobility is limited by the defect concentration. Diffusion coefficients, D , typically assume values in the range of 10^{-11} to 10^{-8} cm^2/s . For example, solid NaCl has $7.5 \cdot 10^{-11}$ cm^2/s at 550°C and $5 \cdot 10^{-9}$ cm^2/s at 750°C , the exact values depending on the impurity level. At increasing temperature, yet well below the liquidus temperature, an abrupt increase (cross-over) of the temperature coefficient of D from impurity to thermally induced defect formation is observed. This cross-over must not be mistaken for liquid phase formation. In the liquid state, values of 10^{-6} cm^2/s are typical. Since defect (or better: free volume) formation now becomes less important, the temperature coefficient of D is determined by the ionic motion alone, hence, becomes smaller again. This second cross-over indicates the formation of liquid phase. Figure 2.2 illustrates the behavior for KCl salt (for lack of a curve for NaCl), and contrasts it to the conduc-

tivity measured in a melting mass glass batch.

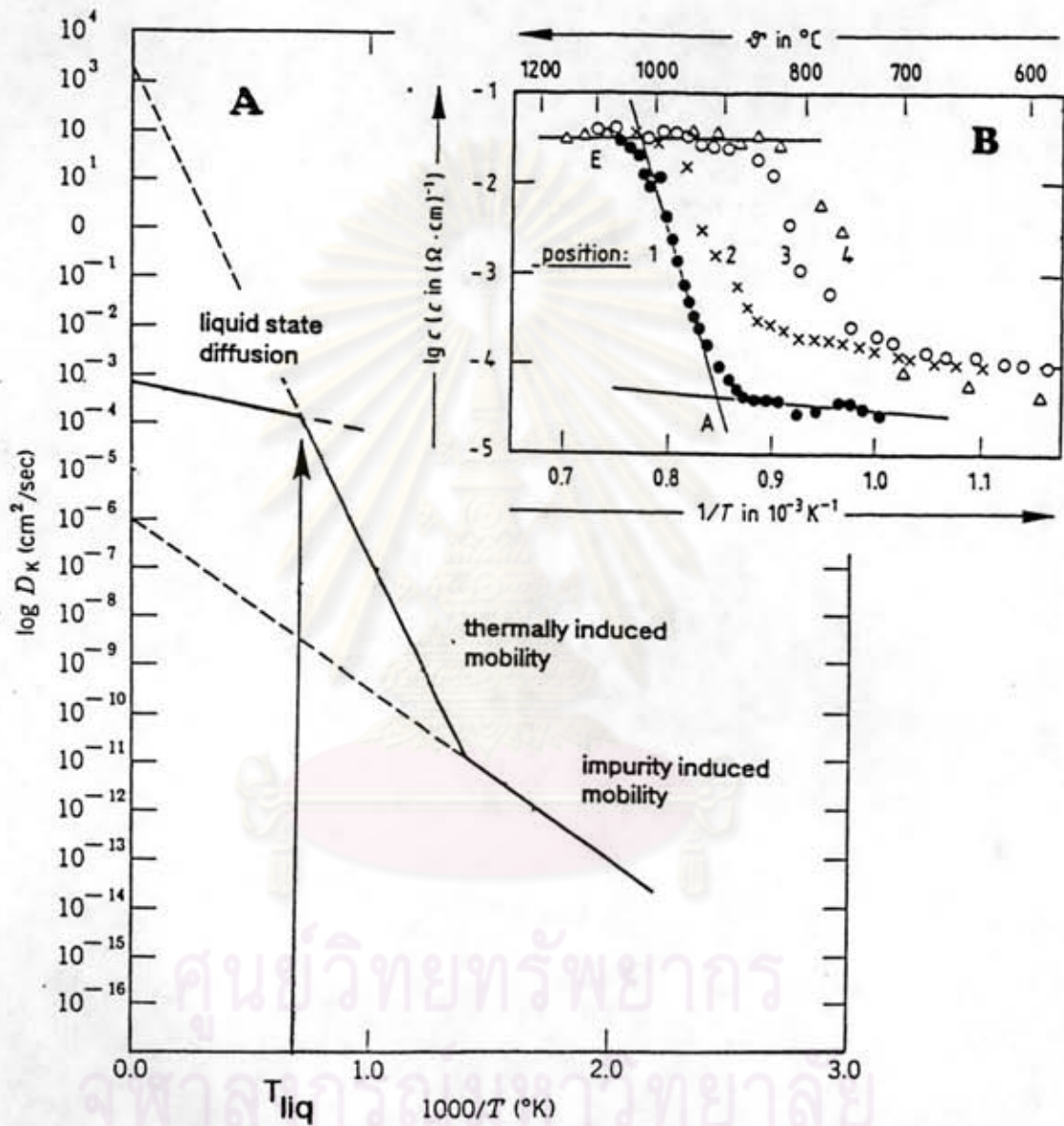


Figure 2.2 A) Diffusion-temperature plot for KCl with 10^{-5} atom fraction divalent cation impurities (KINGERY, 1991). B) Arrhenius plot of electric conductivities at positions 1 to 4 of a batch heap. The tangent construction for position 1 illustrates the determination of onset(A) and (E) of primary melt formation (CONRADT et al, 1994).

In a heterogeneous multiphase system like a batch heap, the situation becomes more complex. In addition to the mentioned mechanisms, electrical conductivity becomes also limited by grain-to-grain contact. Sintering of the solid grains is expected to yield some increase already, which is further enhanced by the local occurrence of isolated portions of liquid phase. The most significant conductivity increase, however, is expected when an interconnected liquid film is established, followed by a slight further increase when the volume fraction of liquid phase grows. The joint effect of ionic mobility and grain-to-grain contact may lead to conductivity-temperature functions which are difficult to interpret in detail. Yet, the point where the conductivity increase by three to four orders of magnitude is terminated can be taken as an unambiguous indicator of an established interconnected liquid phase (see figure 2.2).

2.2 Further generation of liquid phase

The stage when primary melt has formed is characterized by the presence of unreacted original batch constituents, intermediate crystalline reaction products, and melt. There are two kinds of melts that can be produced in the batch: ionic low-viscosity melts and glass forming melts with much higher viscosity. Hence, three basic situations can occur: (i) presence of molten salts without glass forming melt, (ii) presence of glass forming melt without molten salt, (iii) presence of both melts. These two types of melts are partly mutually soluble. As said before, viscosity of inorganic salts is of the order 0.1 dPas, whereas the viscosity of molten silicates and borates is about six orders of magnitude

higher. Figure 2.3 shows several liquid phases that can occur in soda-lime-silica glass batches during heating.

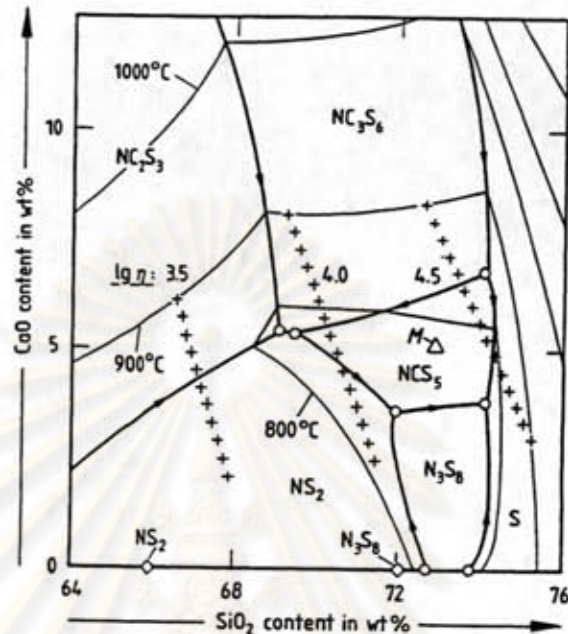


Figure 2.3 Ternary phase diagram of Na₂O-CaO-SiO₂, viscosity levels are also shown.

Formation of melt is usually a heat transfer controlled process that proceeds in batches more easily than processes involving diffusion. Liquid assists reactions of solids by dissolving them and transferring ions more rapidly. Therefore, when the first melt occurs, the reaction increases dramatically (Kroeger 1952, 1957).

When liquid is present, reaction kinetics become more complex than those in solid state mixtures because a larger number of factors effects the transfer mechanism. Some primary melts readily wet solid phases, until their surfaces are completely coated. Precipitating solid products reduce the amount of melt and a large number of tiny precipitated crystals hold the melt and obstruct its

mobility. Reduced fraction of melt means thinner liquid films enhanced due to shorter diffusion distances. If gaseous products evolve, liquid is stirred, which enhances diffusion, but gas may also separate liquid from solid, thus inhibiting reaction. Finally, a combination of steep concentration gradients within the liquid phase and a large gas-liquid interface area introduce surface tension gradients that drive additional convection.

As the amount of melt increases, batch volume initially decreases because of sintering and pulling solid particles together by melt bridges. Heat conductivity of the batch is increased due to melt bridges between solid particles, but is reduced again when foam develops. The individual stages of primary melt formation (conductivity jump) and heat conductivity increase are shown in figure 2.4.

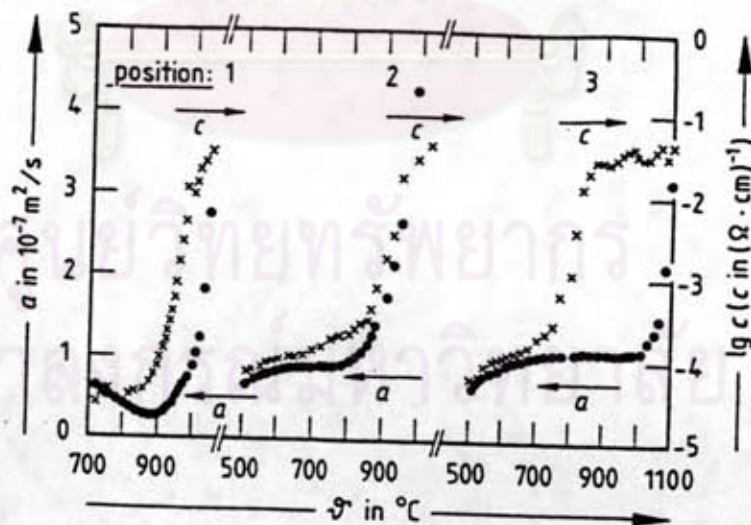


figure 2.4 Electrical conductivities c and thermal diffusivities a (Conradt, 1994).

Unless the batch size is very small, or the batch is percolated by other gases, or melting proceeds in a fluidized state, the reaction atmosphere is that of the reaction gases. In a reducing batch containing coal, O_2 migration into the batch may play a role, though. These gases can initially freely escape through open pores. When the percolation limit is exceeded with a further increase of the amount of melt, batch porosity becomes closed. If gases still evolve and melt viscosity is high, the material acquires a foamy structure with a volume that can many times exceed its original value. Eventually, the foam collapses, all solid particles except some refractory grains are dissolved, and the process enters its final stage.

2.3 Effect of minor additions

The lowest temperature at which melt occurs can be reduced by minor additions of fluxes. As a prerequisite, such a minor addition must not form a solid solution with any of the main components. Ginstling and Fradkina (1952) describe a scenario at which such a minor addition of melting agent operates. Consider the binary phase diagram of sodium carbonate and an inorganic salt (the melting agent) that does not react with silica (see figure 2.3). At a constant temperature between the eutectic temperature and the lower melting temperature of either salt, the equilibrium mixture will consist of solid sodium carbonate and a melt containing all the inert salt (present only in a small quantity), saturated with sodium carbonate (point A in figure 2.5). If silica particles are present, both solid and dissolved sodium carbonate react with silica

producing crystalline sodium silicates. At the same time, solid carbonate dissolves in the melt to compensate for the loss from the melt due to reaction with silica. Thus, the melt acts as a mobility bridge between otherwise less mobile reaction partners. The overall reaction rate depends on the fraction of the wetted silica surface. The amount and composition of melt remain constant at this stage.

After the solid carbonate disappears, the melt becomes impoverished in carbonate until the point of saturation by the inert salt (point B in figure 2.5) is reached. Then the melt composition remains constant due to crystallization of the inert salt. When all carbonate is finally consumed, the mixture consists of unreacted silica, crystals of the inert salt, and crystalline silicates.

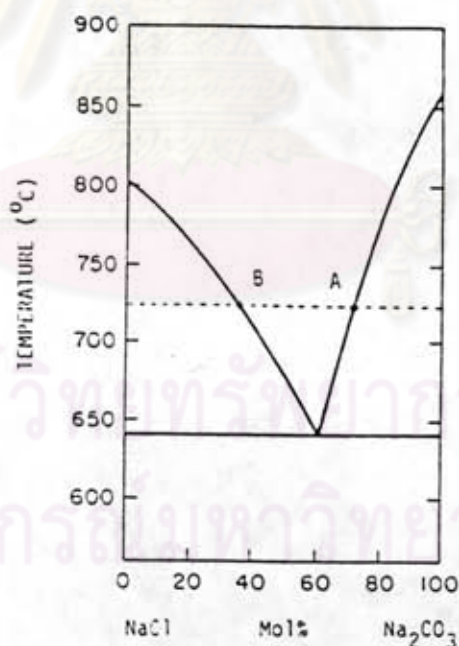


Figure 2.5 NaCl-Na₂CO₃ phase diagram

The rate-controlling process is most likely diffusion of sodium carbonate through the melt. Very little is known about the spatial configuration of melt, silica grains and different



crystalline phases during the process. It is certainly a dynamic situation, because evolving carbon dioxide continuously disturbs the mixture.

Thomasson and Wilburn (1960) showed by thermoanalysis (heating rate 10 K/min) that if the sodium carbonate-silica batch (with 150-200 μ m grains of both components) contained 2 mol% NaCl, the temperature of the maximum mass loss rate decreased by 55 K (from 845 $^{\circ}$ C without additions, see figure 2.6).

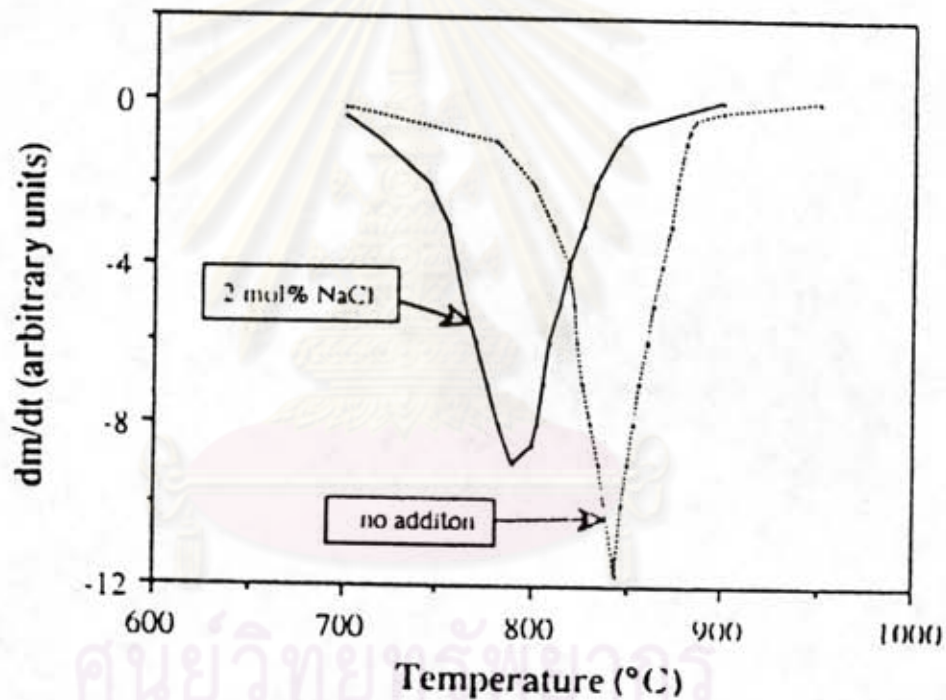
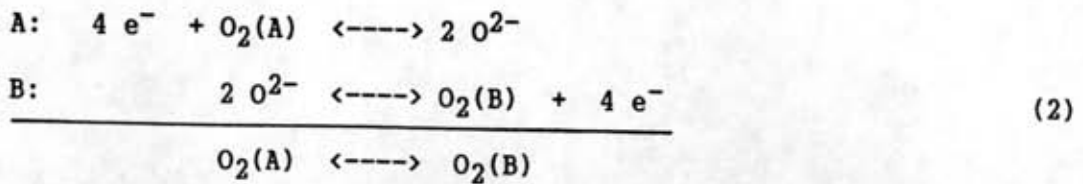


Figure 2.6 Rate of mass change against temperature for quartz-sodium carbonate mixture (15 % NaCO_3 , both materials of grain size 150-200 m; heating rate 10 K/min) with and without addition of NaCl.

If NaF was used, the temperature drop was 85 K. In a batch with less than 50 μ m grains, the drop (from 790 $^{\circ}$ C without additives) was even larger: 135 K in the case of NaCl and 90 K in the case of

where ΔG_0 is the Gibbs free energy of formation of the reactions



Since the turn-over in this reaction is $4 e^-$, $z = 4$ has to be inserted in equation (1). When we assume that the only conduction mechanism in the solid ZrO_2 electrolyte is O^{2-} conduction, then the diffusion potential \mathcal{E}_{diff} can be neglected:

$$\mathcal{E}_{diff} \ll E_0 \quad (3)$$

Finally, the thermovoltage can be approximated by

$$\mathcal{E}_T = s \cdot [T(A) - T(B)] \quad (4)$$

Numerically, the following values have to be used:

$$F = 96500 \text{ As/mol (equivalent to 1 mol elementary charges),}$$

$$R = 8.314 \text{ J/(mol}\cdot\text{K),}$$

$$s = -440 \text{ V/K,}$$

$$a(O_2, B) = 0.21 \text{ if air is used as reference.}$$

Note that $1J = 1 \text{ VAs}$. Now, for E_0 , the following relation holds:

$$E_0 = \frac{R \cdot T(A)}{4 \cdot F} \ln a(O_2, A) / 0.21^b + s \cdot [T(A) - T(B)] \quad (5)$$

with $b = T(B)/T(A)$, T in K. Resolving for $a(O_2, A)$ yields

$$\ln a(O_2, A) = b \ln 0.21 + \frac{4 \cdot F}{R \cdot T(A)} (E_0 - s \cdot [T(A) - T(B)]). \quad (6)$$

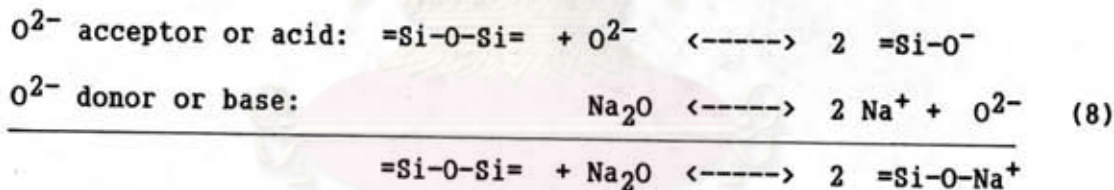
The oxygen activity $a(O_2)$ can be identified with the partial pressure of oxygen $P(O_2)$. For example, when a glass melt is equilibrated with an atmosphere containing 0.001 bar oxygen, then the value of $a(O_2)$ in the melt is 0.001 (no units).

2.4.2 Oxygen in glass melts:

Oxygen in glass melts is involved in two fundamental equilibria. This is, firstly, the *acid/base* equilibrium



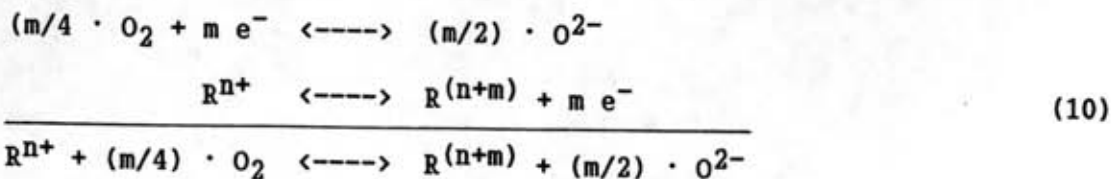
which determines the degree of dissociation of chemically dissolved oxygen from its metallic counter ions. In a sodium silicate glass, this reaction can be specified as



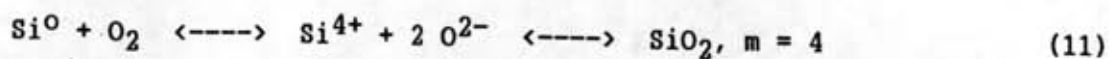
The other fundamental equilibrium is the *redox equilibrium*



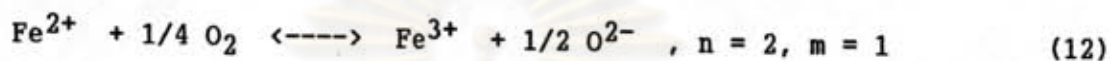
which determines the ratio between chemically dissolved free oxygen O^{2-} and physically dissolved oxygen O_2 . The reaction is either part of the formation reaction of an oxide, or is complemented by a valency change reaction of a polyvalent ion. In general, this reads



when $n = 0$, then deal with a formation reaction, such as

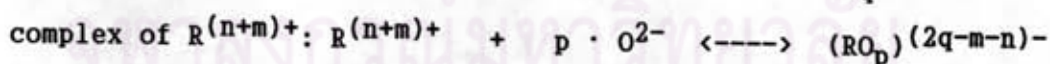
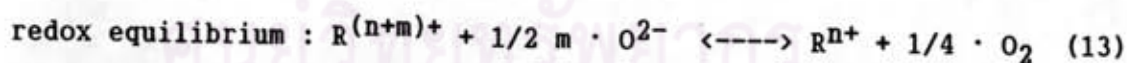


otherwise with a valency change reaction like

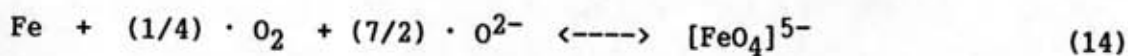


2.4.3 Interaction between oxygen and iron:

In industrial glasses, there are always polyvalent ions present. In this case, the acid/base equilibrium and the redox equilibrium interact. This interaction occurs because the individual valency states of the polyvalent ions dissociate from their oxygens differently. The undissociated forms can be understood as oxygen complexes.



The most important polyvalent element contained in practically all industrial glasses is Fe. The Fe^{2+} is quite basic and is mainly dissociated from the oxygen complex:



In mass glass with average basicity (i.e., with technically

typical amounts of Na_2O , K_2O , and CaO), the thermodynamics of the equilibrium can be described by

$$a(\text{O}_2) = K_p^2 \cdot \left[\frac{\text{Fe}^{3+}}{\text{Fe}^{2+}} \right] \quad (15)$$

with the equilibrium constant K_p given by CHOPINET (1986) as

$$K_p = 13.1 - 29000/T, \quad T \text{ in K.} \quad (16)$$

From a practical point of view, the redox state of glass can be set by controlling the redox number R of the batch. The empirical relation

$$\frac{\text{Fe}^{2+}}{\text{Fe}^{2+} + \text{Fe}^{3+}} = 0.4 + 0.015 \cdot R \quad (17)$$

holds surprisingly well. By combining equations (6), (15), (16), and (17), relations among the quantities E_0 , $a(\text{O}_2)$, $\text{Fe}^{2+}/\text{Fe}^{3+}$ are obtained.

The redox number R is directly calculated from the batch composition by

$$R = \sum m_j \cdot R_j \quad (18)$$

where m_j is the amount of the raw material j per 2000 kg sand, and R_j is its redox increment. The following table gives the increments R_j for some of the most important redox-active raw materials. Common

raw materials such as soda ash, limestone, dolomite, feldspar, sand are approximated by $R_j = 0$.

Table 2.1 Redox factors R_j of redox active batch additions

raw material	formula	R_j per 2000 kg sand
carbon	C	- 6.70
fluor spar	CaF ₂	- 0.01
iron red	Fe ₂ O ₃	+ 0.25
chili saltpeter	NaNO ₃	+ 0.32
salt cake	Na ₂ SO ₄	+ 0.67
arsenic	As ₂ O ₃	+ 0.93
manganese oxide	MnO ₂	+ 1.09

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