Chapter II

Theoretical Part

Thermodynamics of batch melting

The 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.

A. Direct melting

The most straight-forward way of primary liquid phase formation is direct (physical) melting. The melts has low viscosity typical of ionic melts, allowing them to rapidly fill in voids in the batch. An alternative case of direct melting is the melting of cullet. Cullet melt has high viscosities. Cullet does not melt at a specific temperature, but by gradual softening.

B. Sulfate reduction

Sulfate reduction occurs under distinctly reducing conditions yielding Na_2S. Due to forming of eutectic, the temperature is among the lowest liquidus temperatures possibly established in mass glass batches.

C. Reactive carbonate melting

Carbonates typically present in mass glass batch are soda ash, limestone, and dolomite. Upon heating-up, they will decompose to CaO and CO_2. However, Na_2CO_3 and $CaCO_3$ form a low-temperature eutectic at 785°C located between the reaction point of $Na_2Ca(CO_3)_2$ at 817°C and pure Na_2CO_3.
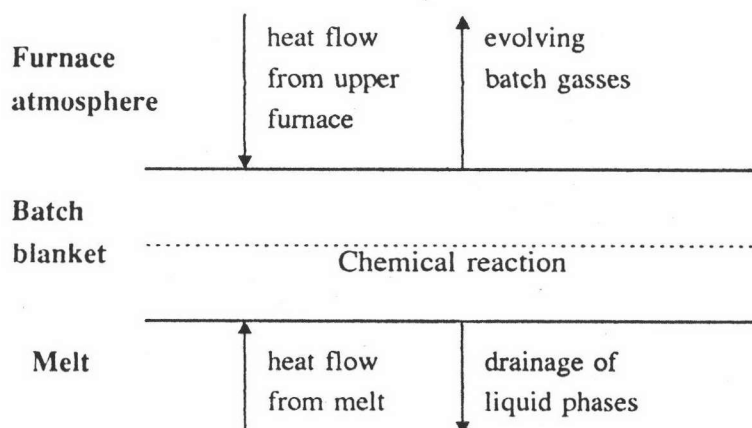
D. Reactive silicate melting

The direct melting between SiO_2 and $CaCO_3$ is of little significance for the overall reaction rate. However, with a soda-lime melt already present, a reaction of the type below take place.

$$\text{soda-lime melt} + SiO_2 \rightarrow Na_2O\text{-}CaO\text{-}SiO_2 \text{ melt} + CO_2 + \text{solid silicates}$$

The "silicate route" start with a reaction between SiO_2 and Na_2CO_3. This reaction typically occurs as a solid state reaction already and proceeds according to the pattern $Na_2CO_3 + nSiO_2 \rightarrow Na_2O \bullet nSiO_2 + CO_2$ with n=1/2,1,2,3. Thermodynamic stability of the silicates increases along with n.

Macroscopic batch melting

Batch melting is heated in many models as a quasi-stationary and quasi-isothermal process during most of the melting time. Then we can treat the batch melting as a heat flow coupled to a mass turnover rate by the thermochemistry of melting reaction, and a mass flow coupled to the mass conversion rate by the fluid mechanics of the generated melt. Therein, the mass turnover acts as a heat sink and a source of drainable matter. The idea is sketched below.

Furnace atmosphere	heat flow from upper furnace ↓	evolving batch gasses ↑
Batch blanket	.... Chemical reaction	
Melt	heat flow from melt ↑	drainage of liquid phases ↓

Temperature profile

After Fuhrmann, 1973 (computer simulation), the batch melting process assumes as a stationary state throughout more than 90% of the batch melting time, and the batch blanket can be treated as isothermal surface in good approximation (shown in figure 2.1,2.2)
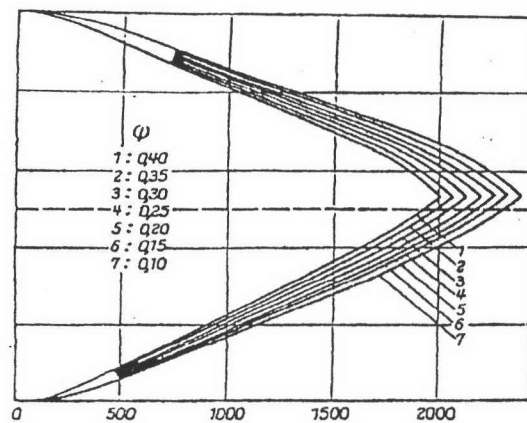

Figure 2.1 Temperature profile in the batch blanket (Fuhrmann, 1973)
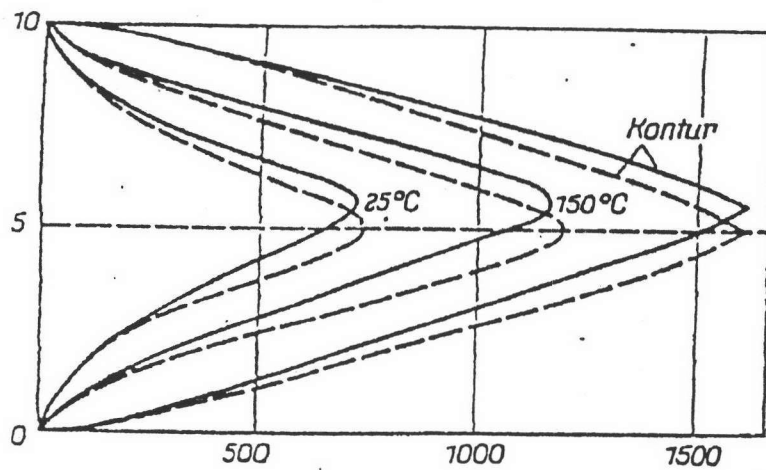

Figure 2.2 Melting front of batch blanket (Fuhrmann, 1973)

We assume that the batch blanket takes a temperature equal to the liquidus T_R of the resulting glass or sub-system. T_R can be determined by consulting phase

diagrams, or by the system given by Backmann et al (1990). The batch melting thus proceed at a constant rate r_b,

$$r_b = (1/A_b) \cdot (dm/dt) = constant$$

A_b = area of batch blanket, m = mass of primary melt formed

Some of the basic assumptions of the model (e.g., isothermal melting) are not confirmed by experiment. Nevertheless, such calculation give valuable guidelines.

Data reading

A. Thermocouple and electrode

1.) Thermocouple

A thermocouple is a device consisting of two solid junctions between two different kinds of metal A and B. The single junction looks like this:
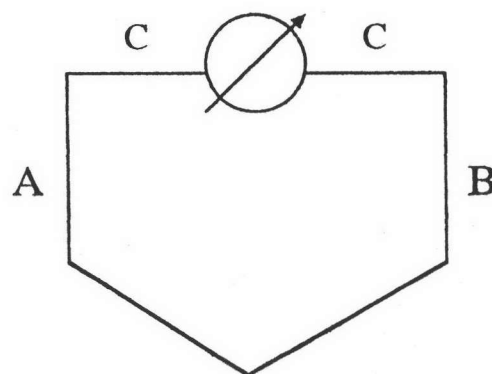
Note that any practical use of such a single junction involves at least two further solid junctions to the metal C of the measuring device. Since the step of the electric potential A-C is different from B-C, the use of a single junction element

is always a compromise with respect to accuracy. If we use, however, a thermocouple, then a symmetric transition to the metal C is possible, and no contact voltage other than that occurring at A-B is involved.

There are different types of thermocouple. For all of them, the mV vs. temperature in $^{\circ}$C values are tabulated with reference to the ice point.

2.) Electrode (electrical conductivity)

Electrical conductivity is chosen as the local indicator of the first occurrence of liquid phase. 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 depend on the free space available for the ionic motion (defect concentration, free volume) and on the activation energy of the motion it self. As the Na^{+} ion is the predominant charge carrier in commercial batch composition, the behavior of sodium salts in general is discussed. In the solid state, ionic mobility is limited by the defect concentration. At increasing temperature, yet well below the liquidus temperature, an abrupt increase of the temperature coefficient of D from impurity to thermally induce defect formation is observed. This cross-over may not be mistaken for liquid phase formation. Since defect formation now becomes less important, the temperature coefficient of D is determined by the ionic motion alone. This second cross-over indicates the formation of liquid phase. Figure 2.3 shows the relation of the temperature and the diffusion coefficient.
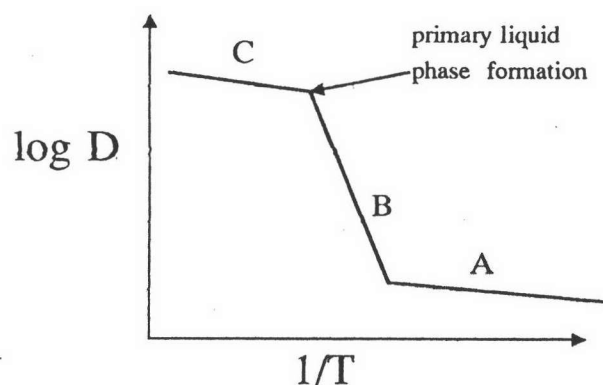
Figure 2.3 Relation of the temperature and the diffusion coefficient

A = impurity effect, B = thermally induced "D", C = liquid phase

The Nernst-Einstein relation allows to an estimate the corresponding conductivity æ in $(\Omega \bullet cm)^{-1}$ by

$$D = (R \bullet T \bullet \Gamma \bullet M) \bullet æ / Z^2 \bullet F^2 \bullet X \bullet \rho$$

R is the gas constant, F is Faraday's constant, T is the absolute temperature, and ρ is the density of the system; X, Z, and M are the molar fraction, charge number, and molar mass of the predominant charge carrier; Γ is the thermodynamic factor of the corresponding component. None of the variables T, Γ, X, and ρ vary except within the same order of magnitude. Thus, a substantial change of D goes along with a substantial change of conductivity.

B. Modes of connecting an analog data signal

Modes of connecting to an amplifier can be separated in three modes. Each mode of connecting will give a different result. Modes of connecting are:

1.) Floating reference input

Since the amplifier has only differential input channels, each input must have two signal wires. The differential input responds only to the voltage difference between the high and low inputs. If the signal source has no connection to ground, it is called "floating source". A connection must exist between low and ground to define a common input voltage for the floating signal source. To measure a floating reference input, the connecting is shown in figure 2.4.
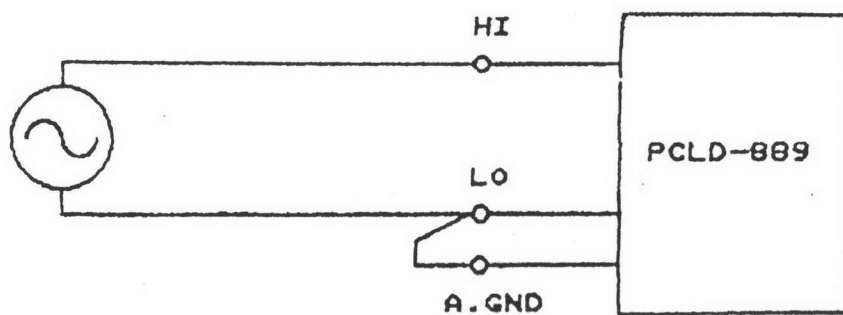

Figure 2.4 Floating mode connection

2.) Non-floating reference input

The signal source has one side connected to a local common ground. The signal source ground and the amplifier ground will not be at exactly the same voltage as they are connected through the ground return of the equipment and building wiring. The difference between the ground voltages forms a common mode voltage. To avoid the ground loop noise effect, the signal ground should be connected to the low input signal. The low input signal should not be connected to the amplifier ground directly. For better grounding, in some cases, a wire connection between the amplifier ground and signal source ground is necessary. Next two figures explain the correct and incorrect connections of a differential input

with local ground. When selecting a suitable ground, it should be avoided by any means to use the zero pole of the ordinary 220 V AC net. This ground carries all kinds of noise from equipment in the same building (mechanical or solid state relays, microwave ovens, transformers, etc.). The best ground is a metallic water pipe. Secondary, connections to ground must have a loop-free topology. Otherwise, the ground loop catches all kinds of electromagnetic noise like an antenna.
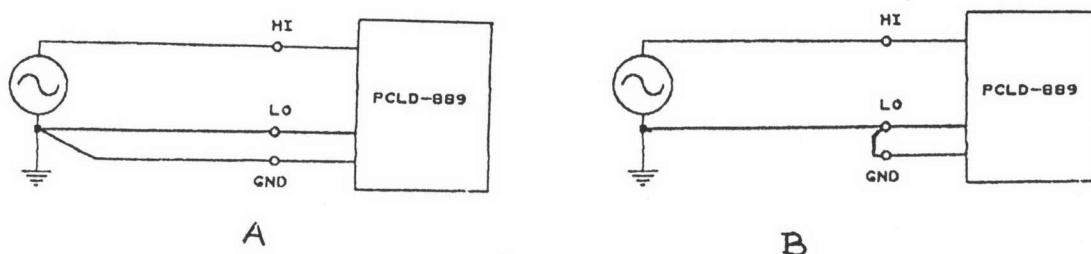

Figure 2.5 Non-floating mode connection

A = Correct connection, B = Incorrect connection

3.) Disconnected ground input

The signal source has one side connect to a ground and the amplifier is disconnect from any ground. Both low and ground are not connected together. This connection will have a noise effect easily because it does not have any reference for the amplifier. Data from this connection always have a high level fluctuation. The connection is shown in figure 2.6.
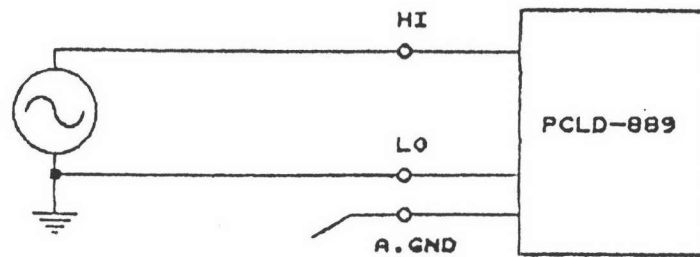
Figure 2.6 Ground disconnected

Data processing

Data processing is the way used to process the raw data. The raw data that come from the fast automatic recording are not smooth. They tend to fluctuate. Data processing is used to smoothen the data. In a commercial voltmeter, this is done by an integration circuit; in old equipment, the inertia of the hand (or pointer) had the same effect.

A. Hardware

Data processing by hardware is very useful to correct the data before they enter the reading process. Resistor and capacitor are used in this application. They are used to cut off undesired the frequencies. From the equation Hz = 1/RC, select R and C so as to cut off certain frequencies. The independent selection of R and C is also necessary. High C can integrate the data for longer time; then we should use a lower R. A high C also results in low imaginary resistance:

$$R_{im} = 1/\omega C.$$

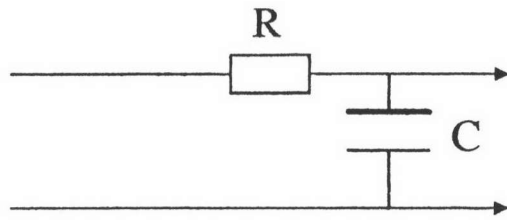A circuit of this application is shown in figure 2.7.

Figure 2.7 A circuit of R and C for the data processing

B. Software

The other way by which data can be smoothed is the software method. This method will smooth the data by mathematical manipulations, such as integration. This method is applied to the recorded data. This method will not work if the input data carry systematic errors, such as very high fluctuation or overflow.