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Temperature Fluctuations in Fractional Solidification of Organics

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Summary

Temperature measurements were made inside zone-melting and progressive-freezing tubes. Short-term fluctuations of up to 3.7°C were found. These resulted from drops falling into the melt, unsteady free convection in the melt and on the outside of the tube, and drafts in the room. We believe that these fluctuations cause impurity striations (banding) and thereby reduce fractionation. Variations of up to 2.5°C over periods on the order of hours were also observed. Long-term variations in temperature and in temperature fluctuations are probably responsible for many of the deviations in impurity content from theoretical predictions.

Fractional solidification is gaining widespread application to the purification of both organics and inorganics (*1*). Theoretical analyses of two popular fractional-solidification techniques—zone melting and progressive freezing—predict that the concentration of an impurity in the treated solid should be a smooth monotonic function of position. In many instances, however, cyclic or irregular variations in composition have been observed (*2–7*). These variations are generally attributed to fluctuations in the solidification rate [e.g., (*8*)]. However, there has been some controversy over the causes of variations in solidification rate in situations in which care is taken to eliminate external effects such as mechanical motion or poor temperature control (*9–10*). A persistent—but unproved—hypothesis has been that intermittent freezing due to constitutional supercooling is the cause (*4,9,10*). However, recent work on high-

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temperature materials has shown that their striations arise from temperature fluctuations due to turbulent or oscillatory free convection (*6,7,9,11–15*).

In the present work, sensitive temperature measurements were made in organic melts to determine if appreciable temperature variations occur in typical experimental arrangements. In the appendix it is shown that temperature changes as low as 0.03°C in the bulk melt or 0.004°C at the freezing interface are sufficient to cause changes of 1 mm/hr in the freezing rate. [Freezing rates on the order of 1 mm/hr are commonly employed for the fractional solidification of organic compounds (*1,16*).]

TABLE 1

Summary of Observed Temperature Fluctuations
(all with no vertical mechanical motion)

Thermocouple position	Long term		Short term	
	Temp. range, °C	Period	Temp. range, °C	Period
Ice bath—test of noise level	0.01	2 min	0.005	~3 sec
Zone melting				
1.6 cm above top of zone in bare tube (Fig. 1)	2.5	1 hr	0.15	3 min
Liquid at bottom of zone in bare tube (Fig. 2); drops falling from vapor space			3.7	Spike
Liquid at bottom of zone (Fig. 2)	1.2	4 min	0.4	5 sec
2.2 cm below zone with bare tube	2.5	1 hr	0.08	3 min
1 cm below zone with outside tube in place	1	2 hr	0.04	1 min
1 cm below zone with bubbled alumina in space between tubes	0.3	1 hr	0.04	1 min
Bridgman				
12 cm above solid–liquid interface, furnace open at bottom (Fig. 4)	0.2	1 hr	0.5	Spike
4 cm above interface (Fig. 5), furnace open at bottom	0.1	20 min	0.04	~1 min
In melt immediately above interface, with furnace open at bottom	0.04	24 min	0.004	10 sec
In melt at interface with tube clamped and packed tight with refractory wool at top and bottom emergence from furnace (Fig. 6)	0.4	~2 hr		

EXPERIMENTAL DETAILS

A modified (*16*) Fisher zone refiner with a 19-mm-o.d. vertical Vycor tube was employed for the zone-melting experiments. Cooling was accomplished by natural convection to an air-conditioned room. Benzoic acid (m.p. 122°C) was used as a test substance.

A Marshall resistance furnace 32 cm high was employed for the Bridgman experiments. The naphthalene–benzoic acid eutectic melt (m.p. 69°C) was contained in a 21-mm-o.d. Pyrex tube inside a 38-mm-o.d. Pyrex tube.

To eliminate possible temperature fluctuations from a temperature-control circuit, we used a constant voltage input for both sets of experiments. This constant voltage was ensured by use of a Sola constant-voltage transformer in series with a variable autotransformer.

The temperature measurements were made with a circuit developed especially for this purpose [described in (*17*)]. The thermocouple, constructed of bare 30-gage copper and constantan wire, was inserted in an ice bath to test the stability of the measuring system. The noise level was less than 0.01°C (see Table 1). The thermocouple was inserted from the top of both zone-melting and Bridgman tubes. The experimental results are summarized in Table 1.

TEMPERATURE FLUCTUATIONS IN ZONE MELTING

Figure 1 shows the temperature fluctuations 1.6 cm above the top of the molten zone. The source of these fluctuations must have been variations in cooling rate from the tube. Blowing on the tube produced similar short-term effects. Fluctuations of smaller magnitude were observed below the zone, indicating that part of them originated from free convection currents in the air from the two-turn nichrome wire heater. A 37-mm-o.d. tube, placed around the zone-melting tube to eliminate drafts, reduced both short- and long-term variations in temperature. Addition of bubbled alumina insulation up to the level of the heater further reduced the long-term variations below the zone (see Table 1).

Figure 2 shows the temperature fluctuations at the near-planar lower solid–liquid interface with no zone motion. The spikes in the temperature recording were found to originate from drops

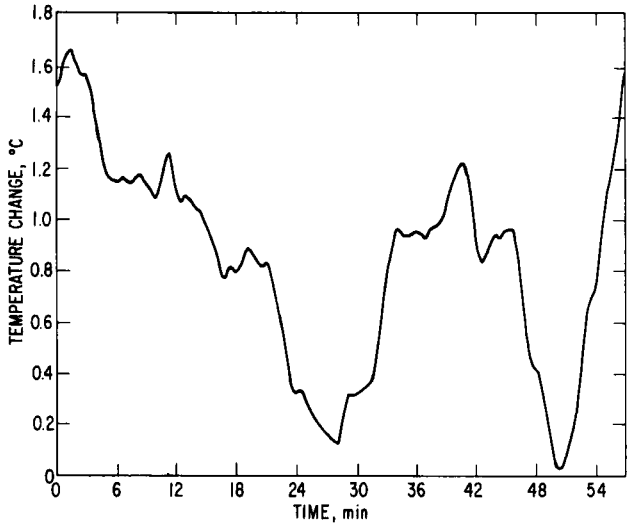

FIG. 1. Temperature in solid 1.6 cm above top of molten zone in uninsulated zone-melting tube; no zone motion.

periodically falling from the upper interface (see Fig. 3). As might be expected, drops fell more frequently when the zone was traveling upward.

We believe the smaller high-frequency oscillations in Fig. 2 originated from oscillations in the free convection flow in the melt. Small particles in the zone showed that the free convection cur-

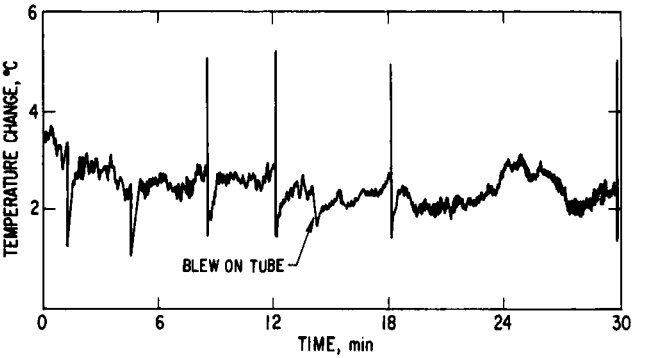

FIG. 2. Temperature at lower solid–liquid interface of molten zone; no zone motion, no insulation. Spikes are caused by drops falling into zone (see Fig. 3).

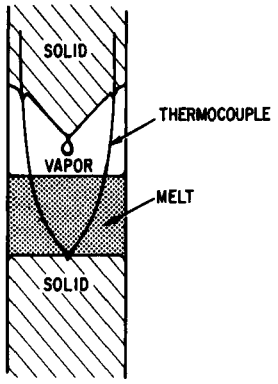

FIG. 3. Appearance of zone during measurements of Fig. 2.

rents, although not turbulent, continually changed position. [Mitchell and Quinn (*18*) have observed similar behavior in completely enclosed gases heated from below.] These temperature fluctuations were more severe in the bulk zone than at the lower interface. Identical results were obtained both with and without the outer tube.

TEMPERATURE VARIATIONS IN THE BRIDGMAN TECHNIQUE

Figures 4 and 5 show the temperature in the melt about 12 and 4 cm, respectively, above the solid–liquid interface with no mechanical motion and with the bottom of the furnace slightly open. To eliminate drafts, we used Fibrefrax insulation to seal the top and bottom of the tube where it emerged from the furnace. In addition, the tube was clamped to prevent any shift in position. Figure 6 shows the temperature in the melt near the freezing

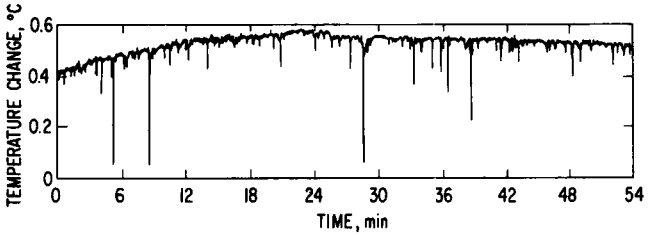

FIG. 4. Temperature in Bridgman melt about 12 cm above solid–liquid interface; no motion.

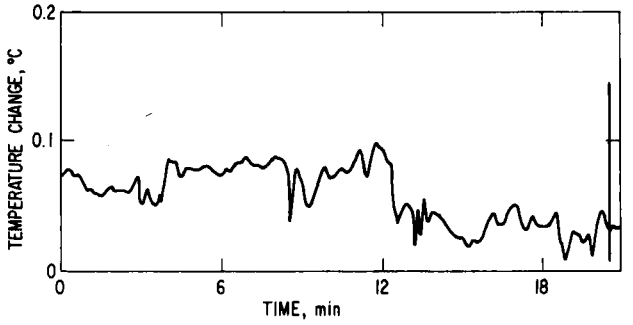

FIG. 5. Temperature in Bridgman melt about 4 cm above solid–liquid interface; no motion.

interface under these conditions. A steady average temperature was never observed. The mean temperature and frequently its direction of drift were altered by a momentary shake of the tube. Shaking had much less effect in the upper than in the lower portions of the Bridgman melt and no effect in the zone-melting experiments. It is probably no coincidence that the fluid is also much more stagnant near the Bridgman solid–liquid interface than it is in zone melting or higher up in the Bridgman melt.

When the tube and thermocouple were lowered at 7.6 mm/hr,

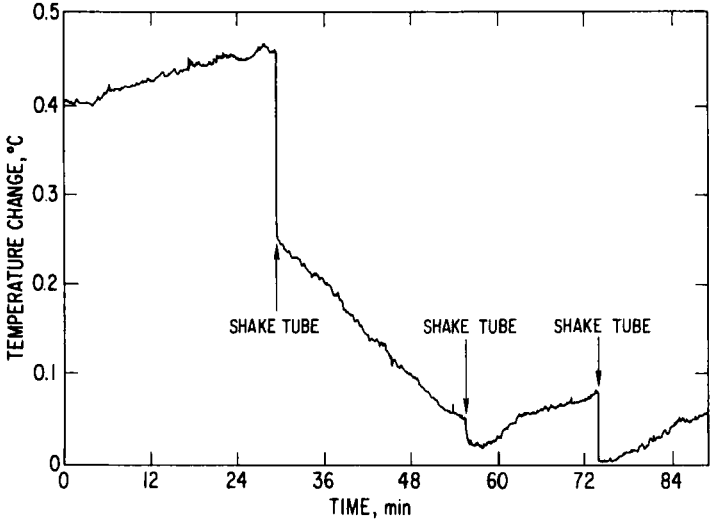

FIG. 6. Temperature just above solid–liquid interface in Bridgman apparatus.

a slightly wavy line was obtained (2.2°C full scale) with occasional 0.06°C bumps. The temperature and interface position continued to change for hours after the lowering was stopped.

DISCUSSION

Both long- and short-term temperature variations were found to be virtually unavoidable in typical zone-melting and progressive-freezing operations on organics under free convection conditions. As shown in the appendix, such variations would cause an appreciable variation in the freezing rate, which in turn would lead to a variation in the amount of segregation (*8*). Thus the high-frequency temperature fluctuations observed here would produce rapid oscillations (striations) in the composition of the treated organic. On a macroscopic scale these striations act to reduce the separation achieved in such an operation [as has been observed with Czochralski growth of CaF_2 (*11*)]. From this standpoint it is as though the true freezing rate were much larger than the average rate one detects externally. [Because of the necessity for diffusion, the separation decreases with increasing freezing rate (*1*).]

The observations recorded here also serve to explain many, if not all, of the larger compositional variations observed in organics (*3–5*). Long-term changes in temperature cause long-term changes in the freezing rate and thereby in the degree of separation. Furthermore, the thermal environment undoubtedly changes during processing. Even aside from external factors (such as variations in room temperature or power input), the free convection currents will be altered by changes in melt geometry and position. If the free convection currents are altered, the character of the temperature fluctuations is also altered, so the degree of segregation changes.

It is well recognized that stirring increases the separation in fractional solidification by reducing the diffusion-boundary-layer thickness (*1,4,19,20*). An added benefit of mechanical stirring is the possible elimination of oscillatory free convection currents, thus producing a more constant freezing rate. For this purpose one can imagine that a steady stirring action is desirable. For example, stirring which is reversed periodically will, in itself, cause oscillating thermal conditions and freezing rates; it is conceivable under such conditions that the separation might even be reduced.

We have observed here that drafts and convection currents on the

exterior of the fractionation container can cause temperature variations, too. Mechanical motion of the container (*21,22*) would reduce or eliminate many of these external effects, which, again, would improve the fractionation.

APPENDIX: ESTIMATION OF FREEZING-RATE FLUCTUATIONS

In the following we estimate the magnitude of temperature fluctuations necessary to affect appreciably the freezing rate and thereby the degree of fractionation. Experimentally, Albon (*23*) found that 0.6°C temperature excursions were sufficient to cause striations in Czochralski growth of InSb. Chase and Wilcox (*17*) observed striations in In_2O_3 due to 0.14°C temperature fluctuations during flux crystal growth. Experimental data are not, however, available for organic compounds. Therefore, we must rely on calculations for our estimate. A fluctuating velocity of 1 mm/hr has been chosen as significant since typical freezing rates are of this magnitude. The results can be easily altered to fit any desired freezing-rate fluctuation.

A heat-transfer analysis (ignoring interface kinetic effects) has shown (*11*) that a temperature fluctuation of ΔT in the bulk melt leads to a freezing-rate fluctuation of

$$\Delta V = \frac{k\,\Delta T}{\rho_s\,\Delta H_f \delta} \tag{A-1}$$

where k is the thermal conductivity of the melt, ρ_s the solid density, ΔH_f the latent heat of fusion, and δ the boundary-layer thickness. Choosing typical values for the parameters, we find that a significant temperature fluctuation is

$$\Delta T = \frac{(1\ \text{g/cm}^3)(34\ \text{cal/g})(0.02\ \text{cm})(0.1\ \text{cm/hr})}{(6 \times 10^{-4}\ \text{cal/sec cm °C})(3600\ \text{sec/hr})} = 0.03°\text{C}$$

Because of the undercooling necessary to drive the freezing process, the interface temperature will oscillate if the freezing rate changes. It is useful, therefore, to estimate the variation in interface temperature ΔT_i corresponding to a variation in freezing rate ΔV. Mathematically this may be expressed by

$$\Delta V = \Delta T_i \frac{\partial V}{\partial\,\Delta T_i} \tag{A-2}$$

The differential is a characteristic of the material being treated. Typical values are

$$V = 0.1(T_f - T_i)^{1.64} \quad \text{cm/sec} \tag{A-3}$$

for benzene (24) and

$$V = 1.56 \times 10^{-5}(T_f - T_i)^{2.3} \quad \text{cm/sec} \tag{A-4}$$

for Salol (25), where T_f is the equilibrium freezing temperature. Inserting Eqs. (A-3) and (A-4) in (A-2) and solving for $\Delta V = 1$ mm/hr yields $\Delta T = 0.004$°C for benzene and 0.6°C for Salol.

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