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T. H. Gouw[a]
[a] Chevron Research Company Richmond, California

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Programmed-Temperature Normal Freezing

T. H. GOUW
CHEVRON RESEARCH COMPANY
RICHMOND, CALIFORNIA

Summary

A normal freezing apparatus is described where the cooling-bath temperature can be programmed between 0.5×10^{-3} and 6.0°C/min. Runs with *n*-hexadecane/*n*-tetradecane test mixtures indicate that improved efficiencies result from programming the cooling bath during the run.

Normal freezing, also known as directional or progressive freezing, is a relatively new purification technique (*1*,*2*). This method complements zone melting and is especially adapted to the preparation of high-purity compounds or the concentration of impurities from substances which are already relatively pure.

The effect of a number of variables in this technique has been studied by, among others, Schildknecht and co-workers. Data have been presented on the effect of initial impurity concentration (*3*), stirring speed (*4*), and speed of crystallization (*5*).

THEORY

The theoretically possible separation is determined by the phase diagram of the relative mixture; the efficiency of the separation is determined by the operating variables of the apparatus.

The ratio between the concentration of impurities in the solid C_S and in the adjacent liquid C_L is described by k, the distribution coefficient. Under ideal conditions and at zero growth rate, $k = k_0 = C_S(e)/C_L$, the e denoting equilibrium conditions. With a finite growth rate at practical operating conditions and for the general case where $k < 1$, k becomes larger than k_0.

Burton et al. (6) have correlated this practical distribution coefficient k to the theoretical value k_0 by

$$k = \frac{k_0}{k_0 + (1 + k_0)e^{-f\delta/D}} \tag{1}$$

The dimensionless quantity, $f\delta/D$, may be regarded as a normalized growth velocity; D is the diffusivity, f the growth rate, and δ the thickness of the boundary layer. For many liquids D lies between 10^{-4} and 10^{-5} cm^2/sec, and δ ranges from 10^{-3} cm for vigorous stirring to 10^{-1} cm for quiescent conditions.

For efficient separations it is necessary to decrease both f and δ, as both D and k_0 are already defined by the system to be separated. It is also evident that, once the minimum values of f and δ have been determined by practical aspects, the most efficient separation is obtained by keeping both f and δ constant.

APPARATUS

A schematic drawing of the improved normal freezing apparatus is given in Fig. 1. The tube which contains the sample is clamped to a precision mechanical drive (Research Specialties, Inc., Richmond, Calif.). Lowering speeds are constant and may be adjusted between 0.01 and 0.4 cm/min. The cooling bath is maintained at a constant level by a large-bore overflow. The position of the stirrer is firmly fixed in relation to the cooling bath, with the stirrer head mounted at approximately the same level as the cooling-bath overflow. The stirrer itself has a specially constructed impeller-type head. A temperature controller keeps the temperature of the cooling bath at the desired level. This controller switches the coolant pump of the auxiliary cooling circuit on and off as soon as the temperature in the coolant reservoir exceeds the preset minimum and maximum values.

In practice, the value of δ depends on the speed of stirring. Because it is adversely affected by fluctuations in stirring speed, it is necessary to use a high-speed motor with speed control.

The value of f depends on the lowering rate of the tube and on the change in heat transfer from the tube to the coolant. Best results would theoretically be obtained by lowering the tube at the lowest possible speed. There is, however, also the necessity to consider a reasonable running time, which for a laboratory-

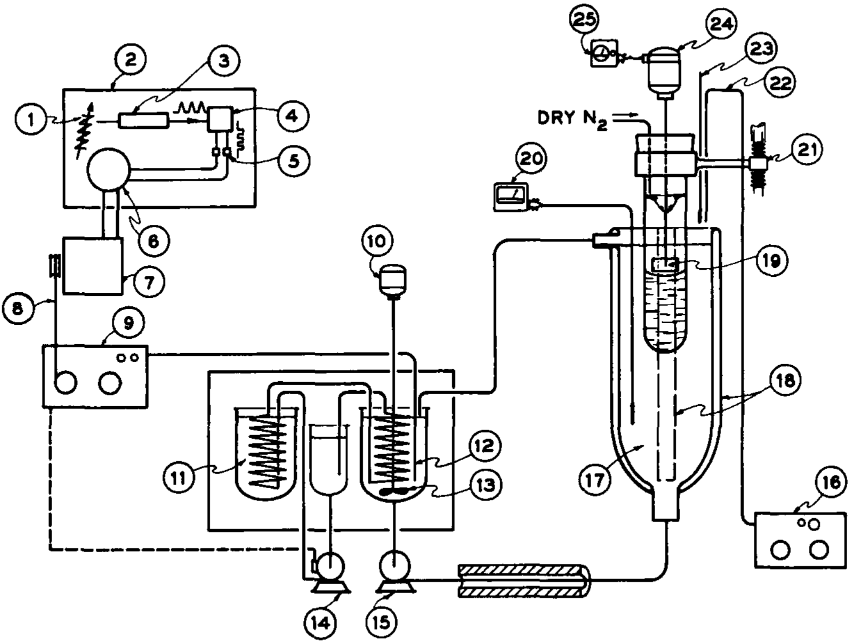

FIG. 1. Programmed-temperature normal freezing apparatus. 1, Rate potentiometers; 2, motion controller unit; 3, unijunction transistor pulse generator; 4, flip-flop circuit; 5, power amplifiers; 6, bidirectional Digimotor; 7, gear box; 8, ratchet; 9, temperature controller; 10, stirrer; 11, CO_2-acetone mush; 12, temperature probe; 13, stirrer; 14, auxiliary coolant pump; 15, centrifugal recycling pump; 16, environmental temperature controller; 17, circulating coolant; 18, silvered Dewar with viewing slit; 19, impeller stirrer; 20, coolant temperature readout; 21, precision mechanical drive, adjustable rate; 22, environmental temperature probe; 23, thermometer; 24, d-c motor; 25, transistorized speed controller and tachometer.

scale setup would lie between 5 and 50 hr. In addition, random fluctuations in the operating parameters would negate any improvement which may be obtained by decreasing the growth rate below a certain speed.

To obtain a constant heat flow from the sample, use is generally made of a constant-temperature bath. This will, however, result in an increase of heat transfer with time because more surface of the tube is exposed to the cooling solution as the run progresses and because the surface exposed to the "warm" air above the coolant decreases with time.

This problem can be solved by programming the temperature of the coolant bath over the length of the run. As this entails a system where the temperature of the bath must rise in the order of a few degrees per hour, the generally available temperature programmers are inadequate for this purpose.

The following system has proved to be useful in our work. A bidirectional Digimotor drives a gear train and gear rack. By setting the rate potentiometers, the output linear speed can be adjusted to any value within a very large range. The rack drives a gear wheel which is mounted on the temperature selector potentiometer of a conventional on–off temperature controller. The programming rate is obviously dependent on the linear speed of the rack and on the type controller. By connecting the rack to the coarse control of a Resistotrol temperature controller (Hallikainen Instruments, Berkeley, Calif.), we are able to adjust the rate of temperature change to any value between 0.5×10^{-3} and 6°C/min. The range most frequently used is 0.02–0.10°C/min.

EFFICIENCY MEASUREMENTS

Test runs were carried out using an *n*-hexadecane/*n*-tetradecane test mixture. This binary system has been proposed for the quantitative evaluation of normal freezing efficiencies (7).

The initial *n*-tetradecane level was 2.00 mole%. The sample size per run was 130 ml; the glass tubes used had an inside diameter of 2.5 cm and were approximately 35 cm long. The stirrer was operated at 2100 rpm. The lowering speed was 0.04 cm/min.

Four runs were performed: duplicate runs with a coolant temperature of −10°C and duplicate runs with a coolant temperature programmed from −12 to 3°C at 0.02°C/min. The freezing point of pure *n*-hexadecane is 18.22°C. Each run is carried out until all material in the tube is frozen. The tube is then removed from the cooling bath and stored for a few hours at −20°C. The glass receptacle is subsequently cut away and the solid material sawed in small sections perpendicular to the longitudinal axis. These fractions are weighed and analyzed by conventional gas chromatography.

Figure 2 shows the results of these runs. The horizontal axis depicts the percentage product crystallized; on the vertical axis is placed the average impurity concentration (*n*-tetradecane) in

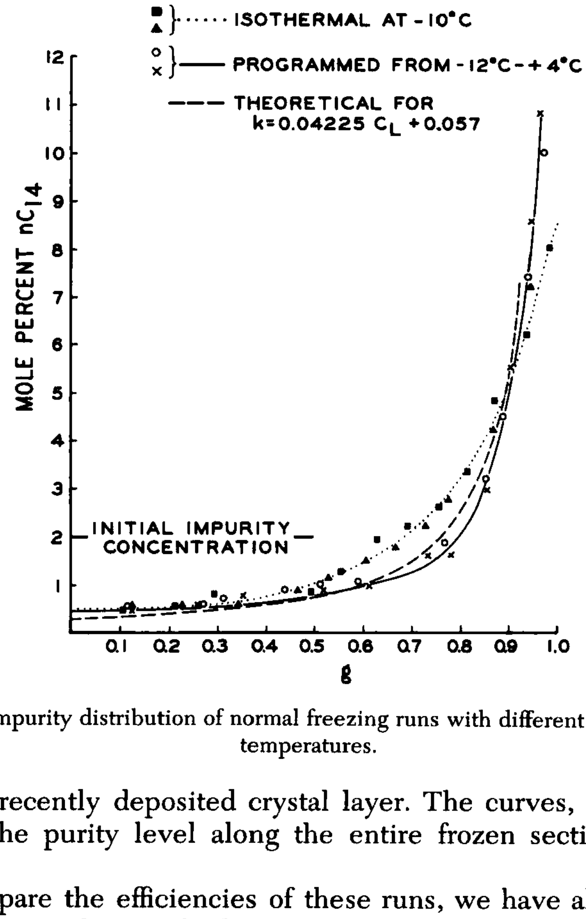

FIG. 2. Impurity distribution of normal freezing runs with different coolant temperatures.

the most recently deposited crystal layer. The curves, therefore, indicate the purity level along the entire frozen section of the sample.

To compare the efficiencies of these runs, we have also drawn in the theoretical curve for $k = k_0$, i.e., for a 100% efficient normal freezing run. This curve has been computed from the earlier derived relations (7).

$$C_L = \frac{1-b}{a + \{[(1-b)/C_0] - a\}\,(1-g)^{1-b}} \tag{2}$$

$$C_S = kC_L \tag{3}$$

$$k = aC_L + b \tag{4}$$

C_L is the average percentage of $n\mathrm{C}_{14}$ in the liquid phase in mole percent, g the fraction solidified, and C_0 the initial $n\mathrm{C}_{14}$ concentration. For the *n*-hexadecane/*n*-tetradecane system we have *a* is 0.04225 and *b* is 0.057.

Up to 60% crystallization, bath temperatures apparently do not have any effect, but as more solid crystallizes out the effect of the programmed-bath temperature becomes apparent. Up to 90% crystallization, the solids obtained by using the programmed-temperature bath show appreciably fewer impurities; the obvious result is that the impurity level in the very last section is very much higher in a programmed temperature run in comparison to that obtained in an isothermal bath.

There is an apparent contradiction in the theoretically computed curve when compared to the curve obtained by temperature programming the run. After 60% crystallization, the theoretically computed curve indicates a higher level of impurities than observed in practice. One should consider, however, that for the theoretical curve the much lower impurity level in the front section of the run will result in a much higher level of impurities in the liquid phase in the middle section of the run as compared to what is obtained in practice. Even with a value of $k_0 < k$, one will find the computed $C_{S(e)}$ to be larger than the observed C_S. With the total amount of impurities constant for all runs, it is obvious that a lower impurity level in the beginning of the run will result in a higher level of impurities in the latter parts of the experiments. The same argument holds for the two sets of experimental data. Crossing of the two impurity distribution curves is, however, observed at much higher crystallization levels.

CONCLUSIONS

Where sufficient starting material is available and where purification is the main purpose, bath temperatures can be either programmed or run isothermally because one can afford to stop at 50–60% crystallization. In many runs it is approximately at the 70% crystallization point that the impurity level of the deposited solid starts exceeding that of the starting material.

In those multipass operations where large yields are desired or in those runs where the objective is the concentration of impurities, programmed-bath temperatures should be used because of the higher efficiencies in the middle to final regions.

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