# ZONE REFINING
## A Student Experiment

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Since its invention by Pfann[1] less than two decades ago, zone melting has become a powerful and important tool for manipulation of impurities in solids[2,3]

Two objectives are served by presenting an experiment in zone refining to chemistry or chemical engineering students. First, an unusual and ingenious separation process is shown based on differences in solubilities of a substance (impurity) between solid and liquid phases. Secondly, modelling of the process reinforces in a new context concepts used to derive the equations for flow tank reactors. The success of the model may then be tested by comparing theoretical and experimental results.

Numerous designs exist of simple apparatuses for carrying out zone refining.[4–7] To the author's knowledge, the following is the only description of a quantitative zone refining experiment for student use. Additional impact is achieved by means of a dye impurity, which produces changes in colour intensity along the length of the ingot.

### DERIVATION OF THE MODEL

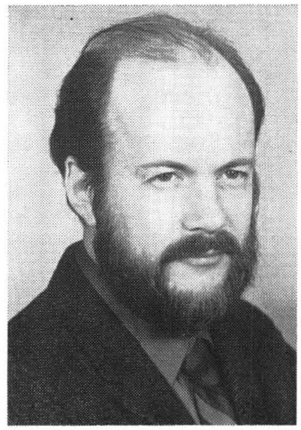
The model will be developed by analogy with a continuous flow stirred reactor familiar to students of elementary reactors. Symbols conventionally used with these reactors will be employed to stress the analogy with the zone refining model. The word **reactor** is used here in a broad sense since zone refining is not necessarily concerned with a chemical reaction.

We assume that the mixture initially contains uniformly distributed impurity. The molten zone, of length $l$ moves through the ingot as shown in Figure 1a, and is idealized to a completely mixed region. Figure 1b shows the analogous model of the continuous flow stirred flow tank reactor (CSTR) with constant input $C_o$.

The transient equation for conservation is

$$\text{Input} - \text{Output} = \text{Accumulation} \qquad (1)$$

For the conservation of mass for the impurity,



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Equation (1) becomes:

$$FC_o - FC_s = \frac{V_o dC_L}{dt} \qquad (2)$$

where $C_L$ and $C_s$ are concentrations of impurity in molten zone* and in solid leaving molten zone, respectively; F is the volumetric flow rate of solids from the molten zone; t is time from the start of operation in either the zone refining region or the normal freezing region—See Eqn. (6); and $V_o$ is volume of the molten zone (constant) in the zone refining region.

Relating equation (2) to that conventionally used to describe transient behaviour of a CSTR, we find two major differences: first there is no output of impurity due to chemical reaction, and second, the concentration within the reactor is $C_L$ instead of $C_s$. However, these two concentrations are related through the distribution coefficient, defined as:

$$k = C_s/C_L \qquad (3)$$

Equation (3) is substituted into equation (2) and the resulting equation is integrated noting that $C_s = kC_o$ at $t = 0$. Furthermore, it is apparent that at any distance x to the edge of the molten zone:

$$\frac{Ft}{V_o} = \frac{x}{\ell} \qquad (4)$$

Thus, we obtain the equation for the zone refining region

*All "concentrations" in this paper are given in dimensionless units, namely g. impurity/g. solute.

$$\frac{C_s}{C_o} = 1 - (1-k)e^{\frac{-kx}{\ell}} \tag{5}$$

When the leading end of the molten zone reaches the end of the ingot, the feed into the molten zone stops, causing a discontinuity in the process. This region is known as the "final zone length" and the process in this region is known as "normal freezing."

Figure 1c shows the decreasing volume of the molten zone, the analogy of which is shown in Figure 1d to be a CSTR draining at constant flow rate.

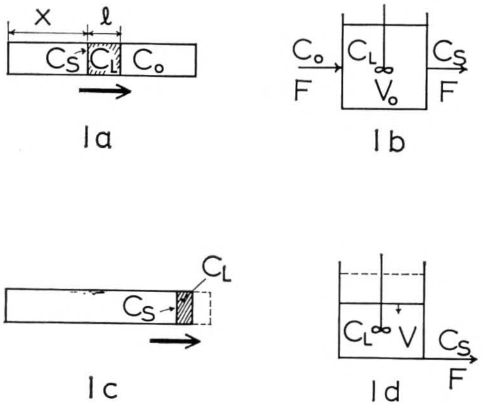


Fig. 1 (a).—Zone Refining Model. (b). CSTR Analog of (a). (c). Normal Freezing Model. (d). CSTR Analog of (c). Heavy arrows indicate direction of zone migration.

Equation (1) for this situation is:

$$0 - FC_s = \frac{dVC_L}{dt} \tag{6}$$

where now, both V, the volume of the molten zone, and $C_L$ are varying with time. For constant speed of the molten zone interface:

$$V = V_o - Ft \tag{7}$$

Combining equation (3) and (7) and introducing the definition

$$1 - \frac{V}{V_o} = g \tag{8}$$

we find that in the final zone length, equation (6) becomes:

$$\frac{C_s}{C_s'} = (1 - g)^{k - 1} \tag{9}$$

Where $C_s'$ = concentration of impurity in solid leaving the molten zone as normal freezing begins. Equations (5) and (9) are now available for correlating the results of zone refining.

## THE EXPERIMENT

The zone refining equipment, shown schematically in Figure 2 consists essentially of an electric heating coil mounted on a motor driven worm and a glass tube containing the acetanilide contaminated with crystal violet dye. Suitable gearing allows the heater to move downwards at 10 cm/hr. This speed was used for convenience in keeping the zone melting process itself to within 1½ hr. This speed is, however, somewhat above the normally recommended rate of 0.3 to 4.0 cm/hr. The glass tube contains a hollow glass tube in the centre. This annular format was used for the zone in an effort to keep the melting and freezing interfaces of the molten zone approximately perpendicular to the direction of movement.

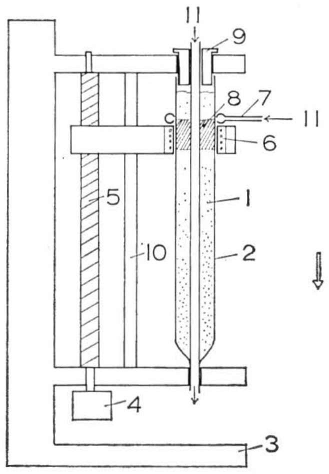


Fig. 2.—Schematic of Zone Refiner. Arrow indicates direction of zone migration. 1. Acetanalide-crystal violet mixture. 2. Glass sample tube with cooling tube in center. 3. Stand. 4. Motor and gear box. 5. Worm. 6. Heater (25-watt). 7. Air cooling jets. 8. Molten zone. 9 .Asbestos plug. 10. Guide rods. 11. Cooling air inlets.

To find the impurity concentration profile of the zone refined ingot, a number of samples are taken from various parts of the ingot, using a scraping tool fashioned by making teeth on one end of a hollow tube fitting into the annulus of the glass tube. In the first and last thirds of the ingot, samples are taken at approximately 0.5 cm intervals, whereas in the centre third, they may be taken at 1 cm intervals. This sampling scheme is followed in view of the expected concentration profile. The samples are then weighed accurately on a chemical balance and dissolved in methanol in small volumetric flasks. The transmittance of each solution is determined, and the calibration curve for the spectrophotometer and the sample weight are used to determine the concentration of crystal violet dye in the acetanilide in the sampled section of the tube. Typical results of this analysis are shown in Figure 3.

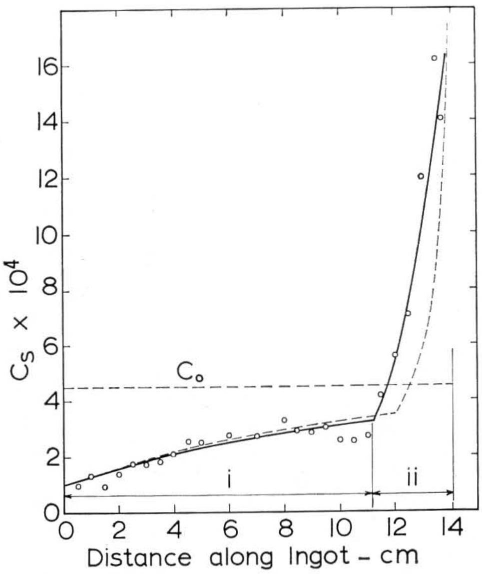


Fig. 3.—Concentration Profile of the Zone Refined Ingot Legend: 0 experimental points; dotted line represents theoretical values using k = 0.20, l = 2.05 cm, $C_0$ 4.5 x $10^{-4}$ g crystal violet per g mixture. i = Zone Refining Section; ii = Normal Freezing Section.

**This experiment introduces an unusual but important separation process and relates it to the analysis of a CSTR.**

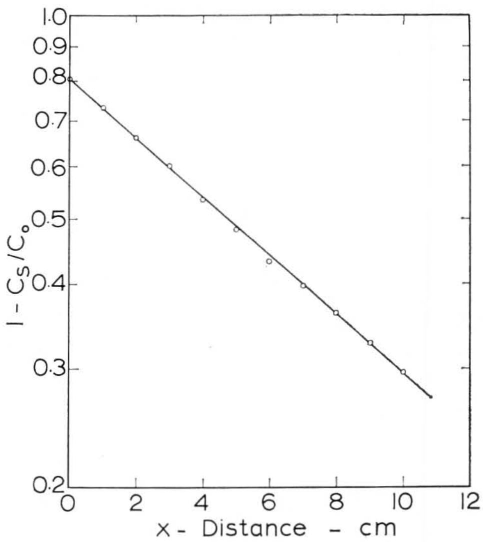


Fig. 4.—Plot of Equation (5) for Zone Refining Section.

## INTERPRETATION OF RESULTS

Figure 3 shows the results of a single pass of the ingot through the zone refining apparatus. The result of a single pass of the zone through the ingot initially at uniform impurity concentration level. The sharp break in the curve indicates the commencement of the final zone length.

In Figure 4, the results of the zone refining section are plotted according to equation (5) in its semi-logarithmic form. It is readily seen that the slope of the line in Figure 4 is equal to $k/l$ and that the intercept is equal to k-1. Thus, both k and $l$ may be determined independently from this measurement.

Figure 5 shows the log-log plot of equation (9). From this equation, the slope is obtained as k-1. However, it is usual to see at least some curvature of the data on this plot; thus, one concludes that the distribution coefficient varies with the concentration of crystal violet dye. Because of the large change of impurity concentration in this region, it is best not to rely on k and $l$ data obtained from the normal melting region, except to qualitatively confirm the model described by equation (9).

Results obtained by two classes of students using equation (5) showed values of k varying from 0.08 to 0.21 while corresponding values of $l$ varied from 1.5 to 4.0 cm. The actual heater length was approximately 2.5 cm; therefore, the results reporting the molting zone to be less than 2.5 appeared perplexing at first. However, upon examining the error structure of equation (5), it can be seen that $\partial l \partial k \approx 10$ cm. A similar value was calculated from the class results. The reason for the variation in the values of $l$ is that the value obtained for k is sensitive to the intercept of the straight line in Figure 4, and the corresponding variation in l is strongly correlated with it, as the partial derivative shows. To reduce the bias in obtaining the intercept in the plot of Figure 4, the data should be fitted by means of a least squares line.

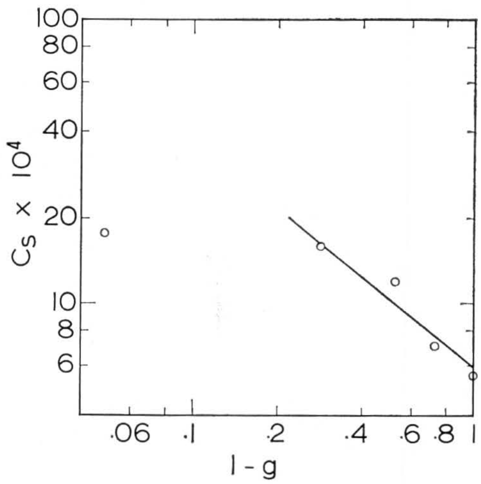


Fig. 5.—Plot of Equation (9) for Normal Freezing Section.

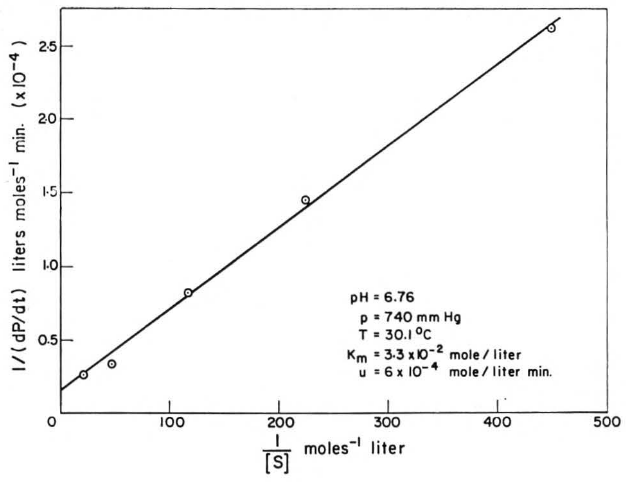


**FIG. 2.—Lineweaver-Burk Plot.**

time and about one hour to perform the calculations.

We have found that although this experiment introduced new concepts to the students, the theory was not beyond their grasp. We were able to present the students with an elementary understanding of biochemical phenomena and arouse interest in a growing area in chemical engineering.

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## ZONE REFINING: HUDGINS

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With a non-uniform impurity profile in the ingot, the solution of equation (2) is no longer analytically tractable. This need not deter further experimentation; indeed, some students may find it worthwhile to compute the results for two or more passes of the molten zone, and test these with experiment.

### SUMMARY

This experiment serves to introduce an unusual but important separation process and provide practice in thinking through a mathematical description of it closely related to that used for flow tank reactors.

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## CONVECTION: Sandall and Mellichamp

**(Continued from p. 136)**

$\rho_{a,\infty}$—density of naphthalene in gas phase in free stream, lb/ft.$^3$
$\mu$—absolute viscosity, lb/hr-ft.
$\nu$—kinetic viscosity, ft$^2$/hr.
$\theta$—time, hr.
Nu—Nusselt number, hd/k
Pr—Prandtl number, $\mu C_p/k$
Re—Reynolds number, $u_\infty d/\nu$
Sc—Schmidt number, $\nu/D_{ab}$
Sh—Sherwood number, $\frac{k'_p d}{D_{ab}}$

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