FOREWORD

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The experimental program was carried out by J. Beutel, Development Chemist, in the Materials Laboratory of the Aeronautical Division, Minneapolis-Honeywell Regulator Company, Minneapolis, Minnesota. Messrs. M. P. Dickey and J. L. Heldenbrand served as project engineer and design liaison engineer, respectively. Dr. V. W. Greene of the Environmental Health Section of the Health Service of the University of Minnesota, Minneapolis, Minnesota served as consultant for the experimental work on micro-organism distribution. The experimental program was carried out during the period 15 April to 15 October 1961. This report is designated as MH Aero Report 2649-TR1.

The author wishes to acknowledge the contribution to this program by Mr. T. M. Crock who proposed the experimental work and made many helpful suggestions regarding experimental procedure and the writing of this report. The theoretical analysis and the distribution curves for multi-pass zone refining are largely taken from the book Zone Melting by W. G. Pfann, with permission from the author.

ABSTRACT

A method of recovering potable water from urine by employing the differences in solute concentration of a liquid-ice phase system as a means of purification is discussed. This method is called reiterative freezing. A parameter of the solute concentration distribution, called the effective distribution coefficient, is defined; and a number of experimental conditions for which the effective distribution coefficient is calculated are described. The effect upon the attainable separation due to rate of freezing, agitation, and direction of freezing with respect to the gravity direction is discussed. The effective distribution coefficients obtained for these experimental conditions are compared with the distribution coefficients attainable under ideal conditions. The effect of freezing upon the distribution of micro-organisms is discussed. The energy requirements for the recovery of potable water from urine by various reiterative freezing schemes are calculated as a function of the yield and of the volume of liquid that must be frozen in order to recover a unit volume of potable water containing less than 500 parts per million of solids. A comparison is made between these energy requirements and the energy requirements of a simple distillation process.

PUBLICATION REVIEW

This report has been reviewed and is approved.

Wayne H. McCandless
WAYNE H. McCANDLESS
Chief, Life Support Systems
Laboratory

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SYMBOLS

C_L Solute concentration in the liquid (grams solute/100 milliliters solution)

C_o Initial or average solute concentration of solution to be purified (grams solute/100 milliliters solution)

$C_{p(\infty)}$ Solute concentration in the product stream in the last of an infinite number of compartments (grams solute/100 milliliters solution)

$C_{p(n)}$ Solute concentration in the product stream in compartment n (grams solute/100 milliliters solution)

C_s Solute concentration in the solid (grams solute/100 milliliters solution)

$C_{w(\infty)}$ Solute concentration in the waste stream, in the last of an infinite number of compartments (grams solute/100 milliliters of solution)

$C_{w(n)}$ Solute concentration in the waste stream in compartment n (grams solute/100 milliliters of solution)

C_x Solute concentration at a distance x measured from the end of the charge at which freezing began (grams solute/100 milliliters of solution)

D Diffusivity of solute in the solvent (cm^2/sec)

f Freezing rate (cm/sec)

f_p Fraction of zone volume transferred each cycle in one compartment of the refiner product stream (dimensionless)

f_w	Fraction of zone volume transferred each cycle in one compartment of the refiner waste stream (dimensionless)
g	Fraction of charge which has been frozen (dimensionless)
ΔH_f	Heat of fusion (cal/gm)
k	Effective distribution coefficient (dimensionless)
k_o	Equilibrium distribution coefficient (C_s/C_L) (dimensionless)
k_1	Effective distribution coefficient obtained from the intercept with the log w = 0 line (dimensionless)
k_2	Effective distribution coefficient obtained from the intercept with the log P = 0 line (dimensionless)
k_3	Effective distribution coefficient obtained from the slope of the linear plot of logw versus log P
L	Length of total charge along axis of freezing (cm)
ℓ	Length of molten zone (cm)
n	The n^{th} consecutively numbered chamber (in cross-flow zone refining)
N	The total number of chambers (in cross-flow zone refining)
P	Fraction of initial concentration at the interface (see Appendix I) (dimensionless)
T	Temperature (°C)
ΔT	Temperature differential (°C)
t	Time (sec)
w	Fraction of charge not frozen, (See Appendix I)(dimensionless)

x	Distance from the initially-frozen end of the charge to the freezing interface (see Figure 4b)(cm)
ρ	Density (gm/cm^3)
γ	Thermal conductivity (cal/°C cm sec)
δ	Thickness of the diffusion layer adjacent to the freezing interface. This layer is at a higher concentration than that of the remaining liquid because of solute rejection at the interface (for $k < 1$).

INTRODUCTION

Present plans to send man into outer space make it necessary to consider the requirements for support of life in space. One of the necessities of any but the shortest flights is potable water. The required supply of water for an entire flight -- approximately 2200 milliliters per man per day (Reference 1) -- might simply be provided from a tank of sufficient capacity. This approach is undesirable for longer voyages, however, because of the large energy required to lift the total weight of water into space and because of the storage volume required in the spacecraft.

Another and more desirable approach for space flights of longer duration is to recover a portion of the water contained in human excretions: urine, feces, and insensible water (perspiration and respiration). Since urine contains more than half of the total amount of water excreted, a number of methods for its recovery have been proposed. Distillation and electrodialysis are among the methods most frequently mentioned. The purpose of this project was to investigate the feasibility of another method: the recovery of potable water from urine by the application of reiterated freezing techniques.

The technique of water recovery by freezing has been extensively investigated and has been applied to salt water purification (Reference 2). Reiterative freezing is effective when the equilibrium concentration of dissolved material (solute) in the frozen (solid) phase of a solution differs from that in the liquid. The operation of a water recovery device based on the principle of reiterative freezing consists of freezing a portion of the solution to be purified (thereby decreasing the solute concentration in the frozen portion) and preventing further mixing of the solid with the liquid phase. The portion containing the lower solute concentration is then refrozen, again preventing phase mixing, and the process is repeated until the desired reduction in solute concentration is achieved.

SECTION I
THEORETICAL DISCUSSION

GENERAL PRINCIPLES OF REFINING BY REITERATIVE FREEZING

The behavior of a two-component, two-phase (solid-liquid) system in equilibrium freezing can best be described by a phase diagram such as that shown in Figure 1. The diagram consists of three regions characterized by two lines called the solidus and the liquidus lines. In the region above the liquidus line, the system is liquid; in the region below the solidus line, the system is solid; in the region between the solidus and the liquidus lines, the solid and liquid phases exist simultaneously.

A solution containing a concentration (C_L) of solute in the liquid is freezing at a temperature T_1, and the crystals of solid appearing as a result of the freezing will contain a concentration (C_s) of solute which lies on the solidus line of Figure 1. If freezing is completed to temperature T_2, all of the solute will be contained in the solid so that, considering the entire mass, C_s is equal to C_L. Under nonequilibrium conditions, however, the solute concentration is not uniformly distributed throughout the solid.

The solution may be visualized as contained within a cylinder, freezing from one end toward the other. If the freezing rate is extremely slow (that is, slow enough to permit diffusion processes to erase any concentration gradients in the liquid and the solid), then the conditions for equilibrium freezing are met. The C_s/C_L ratio is called the equilibrium distribution coefficient, k_o. In equilibrium freezing, the concentration of solute, equally distributed in the solid, is simply equal to the concentration of solute in the initial solution times the equilibrium distribution coefficient. In equilibrium freezing no segregation of solute occurs in the solidified ingot so that, as the fraction of solidified material increases, the solute concentration throughout the ingot increases proportionately until, when all the material has been frozen, the concentration throughout the frozen ingot equals the initial concentration, C_L.

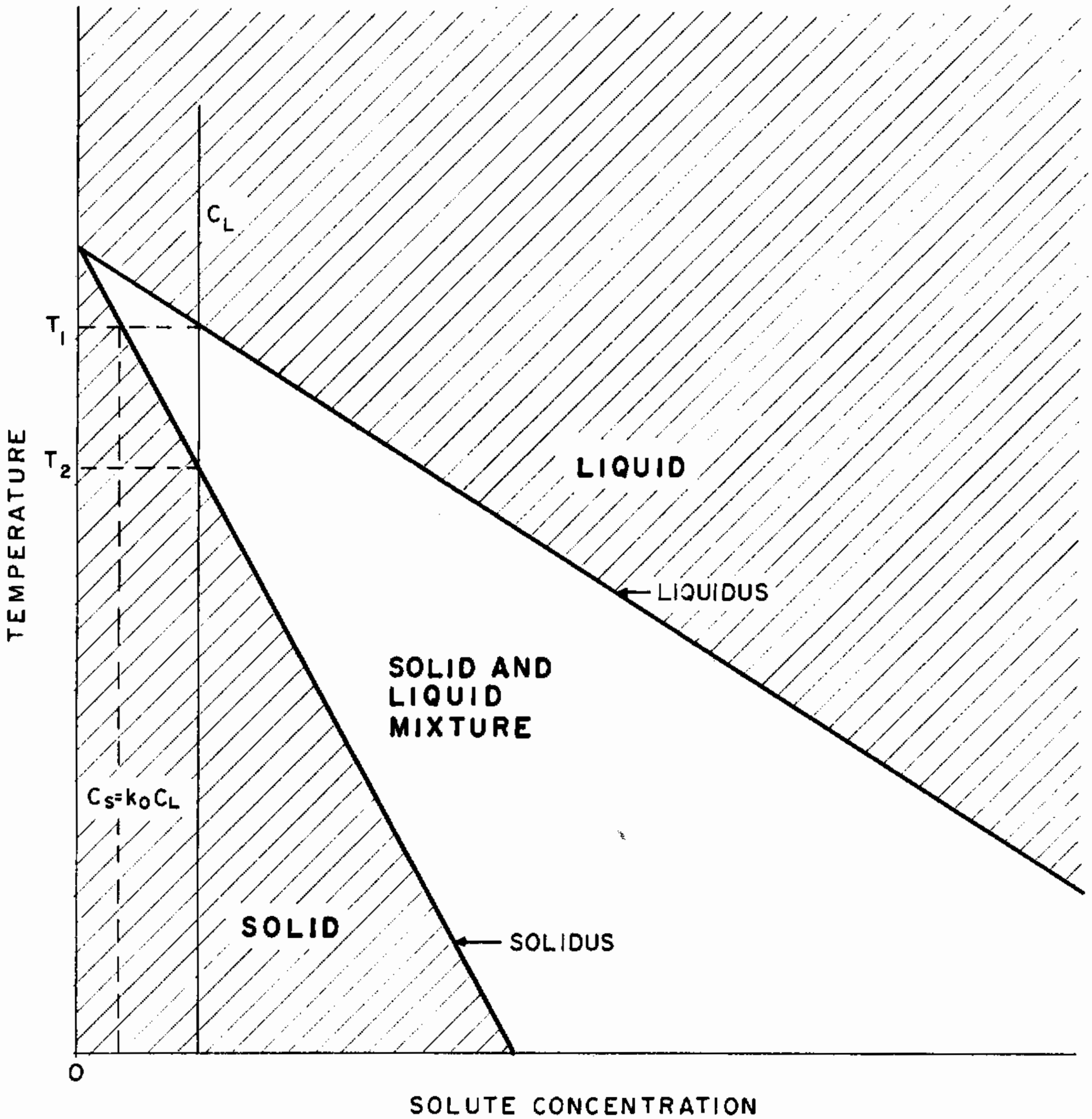


Figure 1. Portion of a Constitutional Diagram in Which the Solute Lowers the Freezing Point of the Solvent

If it is assumed that no diffusion occurs in the solid (which corresponds more closely to the facts), then a concentration gradient is established across the frozen ingot. The amount of segregation which will occur (that is, the magnitude of the gradient) will depend upon the rate at which the freezing interface is allowed to move and the degree of mixing in the liquid.

The assumption that the solute cannot diffuse through the solid, and that the mixing in the liquid is sufficient to give a uniform concentration of solute in the liquid phase at all times, leads to segregation in the frozen ingot which is described by the analytical equation:

$$C_s = kC_o(1 - g)^{k-1\,*} \tag{1}$$

where

C_s = solute concentration in the solid (grams solute/100 milliliters solution)

k = effective distribution coefficient (dimensionless)

C_o = initial or average solute concentration of solution to be purified (grams solute/100 milliliters solution)

g = fraction of charge which has been frozen (dimensionless)

Under the conditions described, and only under these conditions (no diffusion in the solid and perfect mixing in the liquid), the value of the effective distribution coefficient (k) equals the value of the equilibrium distribution coefficient (k_o). In actual experimental situations, where the above two assumptions do not hold exactly, k differs from k_o.

The usefulness of Equation (1) lies in the fact that it may be used to determine values of the effective distribution coefficient from experimental data. Rearrangement of Equation (1) and insertion of parameters which are readily obtainable by experimentation (see Appendix I) lead to the equation:

---

*k is assumed constant with concentration; the density of the solid is assumed to equal that of the liquid.

$$\log_{10} P = \log_{10} k + (k-1) \log_{10} w \qquad (2)$$

where

P = fraction of initial concentration at the interface (see Appendix I) (dimensionless)

w = fraction of charge not frozen, (see Appendix I)(dimensionless)

The following three methods may be employed to determine the distribution coefficient from Equation (2):

a. The intercept of the linear plot of $\log_{10} w$ versus $\log_{10} P$ (as Referenced in Appendix I) with the $\log_{10} w = 0$ ($w = 1$) line is equal to $\log_{10} k$.

b. The slope of the linear plot of $\log_{10} w$ versus $\log_{10} P$ equals k-1.

c. The $\log_{10} w$ value obtained from the intercept of the linear plot of $\log_{10} w$ versus $\log_{10} P$ with the $\log_{10} P = 0$ ($P = 1$) line may be inserted into the equation

$$\log_{10} w = \frac{\log_{10} k}{1 - k} \qquad (3)$$

The plot of Equation (3) is shown in Figure 2.

Method (a) was found to give the most consistent values of the distribution coefficient from the experimental data. The distribution coefficients obtained by this method, designated k_1, are used throughout this report.

Evaluation of the relationship between the effective distribution coefficient and the equilibrium distribution coefficient is also of interest. This relationship indicates how nearly the experimental conditions approach equilibrium (that is, maximum separation of solute).

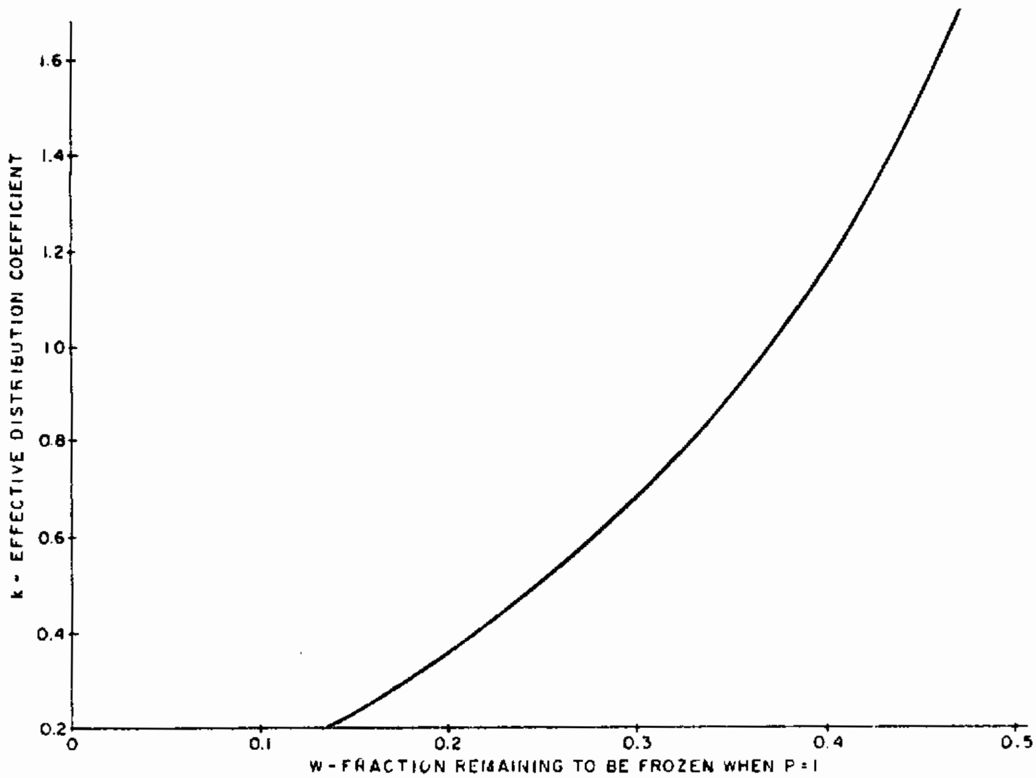


Figure 2. Plot from the Function $(\log w)_{P=1} = (\log k)/(1-k)$

For experiments involving agitation, Equation (4)* allows determination of both the value of the equilibrium distribution coefficient corresponding to an experimentally determined effective distribution coefficient, and the value of $f\delta/D$, which is a relative measure of the efficiency of the agitation process in keeping the solute concentration constant throughout the liquid phase.

$$k = \frac{k_o}{k_o + (1 - k_o)^{-f\delta/D}} \qquad (4)^{**}$$

where

f = freezing rate (cm/sec)

δ = Thickness of the diffusion layer adjacent to the freezing interface. This layer is at a higher concentration than that of the remaining liquid because of solute rejection at the interface (for $k < 1$).

D = diffusivity of solute in the solvent (cm^2/sec)

k_o = equilibrium distribution coefficient (C_s/C_L) (dimensionless)

Equation (4) also allows an analysis of the effect of freezing rate upon the equilibrium conditions provided in the freezing experiment. Rearrangement of Equation (4) leads to the equation:

$$\ln\left(1 - \frac{1}{k}\right) = \ln\left(1 - \frac{1}{k_o}\right) - f\delta/D \qquad (5)$$

When the assumption is made that δ/D is not a function of f, Equation (5) leads to a means of determining δ/D and k_o from experimental data in the following manner: As indicated by Equation (5), a linear plot of $\ln\left(1 - \frac{1}{k}\right)$ versus f yields a line with the slope equal to δ/D. With the value δ/D thus obtained, the $f\delta/D$ values are computed and plotted against the corresponding k values as in Figure 3, which is a plot of Equation (4). Such a plot of $f\delta/D$ versus k gives the value of k_o at the intercept of the curve with the $(f\delta/D) = 0$ line.

*This equation does not apply to the case where the liquid is not agitated.

**Pfann, page 13. (Reference 3).

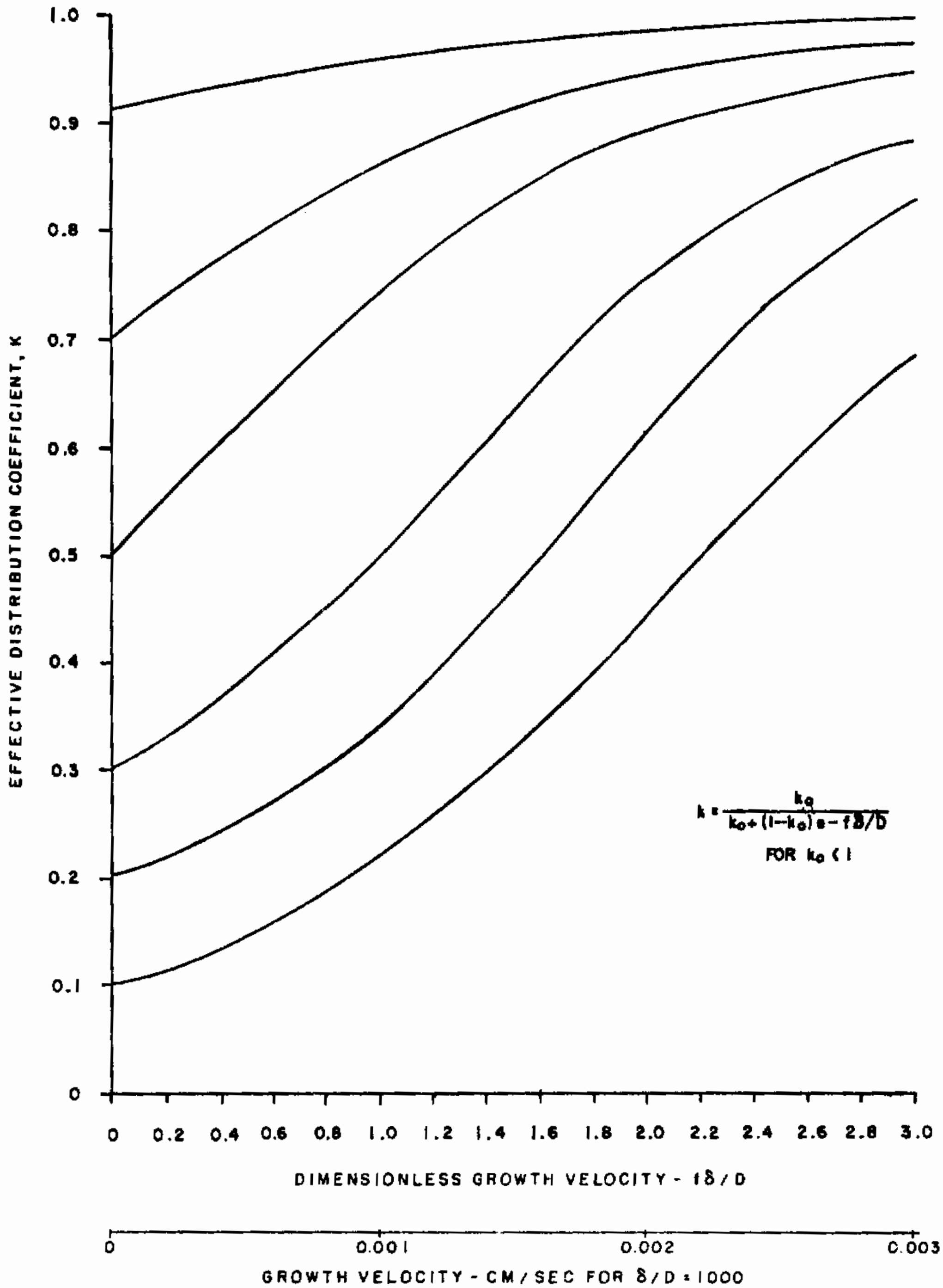


Figure 3. Dependence of Effective Distribution Coefficient on Freezing Rate

The aspects of freezing which have been discussed to this point have allowed definition of a parameter (i.e., the effective distribution coefficient) from experimental data, comparison of this parameter with the equilibrium distribution coefficient for the system under consideration, and estimation of the effect of agitation upon the obtainable solute separation. The magnitude of the effective distribution coefficient describes the degree of separation attained in the freezing process. A low distribution coefficient indicates a large separation. For the purpose of theoretical analysis, it is assumed that the distribution coefficient remains constant during one freezing cycle; i.e., the distribution coefficient is assumed not to be a function of the concentration.

TECHNIQUES FOR PURIFICATION OF SOLUTIONS BY REITERATIVE FREEZING

The simplest technique for reiterative freezing is shown in Figure 4(a). The solution, contained in a cylinder, is allowed to freeze from one end toward the other, and the freezing interface is allowed to move at a constant, finite rate until a portion of the solution has been frozen. When k is less than 1, the frozen portion contains the lower solute concentration, while the remaining liquid contains the higher solute concentration. This type of freezing is called "normal" freezing. Equation (1) describes the concentration gradient obtained from this type of freezing.

A more sophisticated method of reiterative freezing, common to semiconductor refining, is shown in Figure 4(b). Here an ingot with an essentially uniform solute concentration has been formed from the solution. A concentration gradient is established along the cylindrical axis of the ingot by passing a molten zone of predetermined width, at a controlled rate, in one direction only, along the cylindrical axis of the ingot. The distribution obtained after one pass of the molten zone is given by Equation (6).

$$\frac{C_s}{C_o} = 1 - (1 - k)\, e^{-kx/\ell} \qquad (6)^*$$

* Pfann, page 25. (Reference 3)

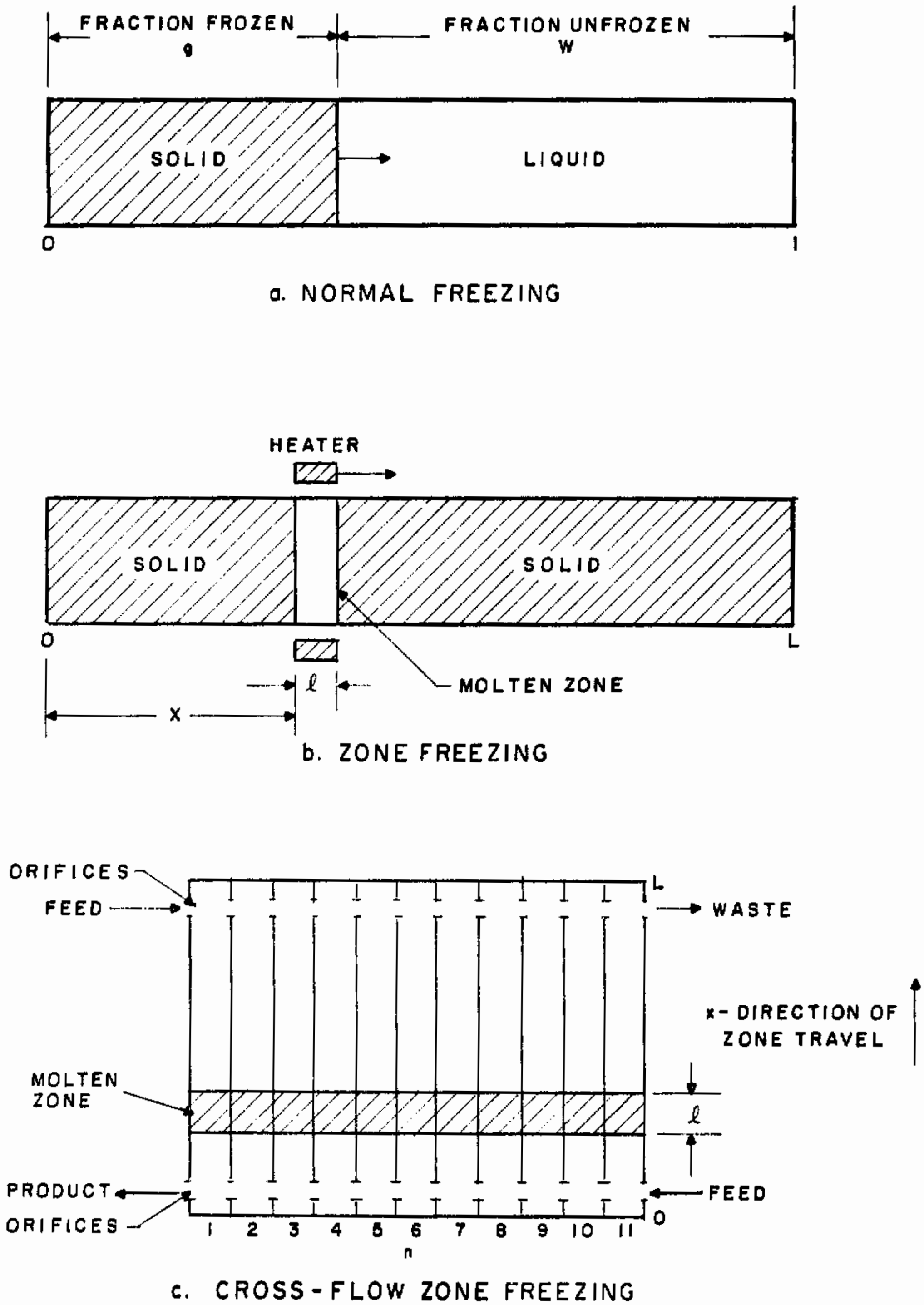


Figure 4. Several Methods of Reiterative Freezing

where

x = distance from the initially-frozen end of the charge to the freezing interface (cm)(see Figure 4b)

ℓ = length of molten zone (cm)

The distribution obtained after an infinite number of zone passes is described by the equations:

$$\frac{C_s}{C_o} = k\, e^{-Bx} \tag{7}$$

where B is a constant.

$$k = \frac{B\ell}{e^{B\ell} - 1} \qquad (8)^*$$

Functions describing the distribution of solute concentration for a finite number of passes are very complex. Rather than list these equations, curves are presented in Appendix II which give the fraction of initial solute concentration versus the distance, in zone lengths, after various numbers of passes for various values of the distribution coefficient.

A third method of reiterative freezing, called cross-flow zone refining,** is diagramed in Figure 4c. Feed enters through two ports at diagonally opposed ends of the refiner. Waste and product leave through another pair of diagonally opposed ends. As two streams, designated the product stream and the waste stream, travel across the refiner in opposite directions, molten zones travel upward, depositing impurity in the upper end of the refiner and purifying the lower end. The refiner itself is divided into a finite number of sections with partitions which are interconnected at both ends by orifices in the region where the product and the waste stream are to flow. When the zones are at the bottom of the refiner, a volume of feed is injected, and an equal volume is

*Pfann, page 41. (Reference 3).

**W.G. Pfann has applied for a patent on this method of refining.

transmitted from one chamber to the next, without mixing, until in the last chamber an equal volume of product is ejected. Similarly, when the zone is at the upper end of the refiner, a volume of feed is injected (upper left corner) and volumes of intermediate solution are transmitted from one chamber to the other until, at the end, an equal volume is ejected as waste.

Figure 5 shows the distribution of solute concentration in the waste stream and in the product stream for this type of refiner. The distribution of product concentration in the product stream is given by the equation:

$$C_{p(n)} = G^{N-n+1} + \frac{C_{p(\infty)}}{C_o} \qquad (9)^*$$

in which

$$G = \frac{f_p}{f_p - \left(\frac{1}{k} - 1\right)} \qquad (10)$$

where

$C_{p(n)}$ = solute concentration in the product stream in compartment n (grams solute/100 milliliters solution)

$C_p(\infty)$ = solute concentration in the product stream in the last of an infinite number of compartments (grams solute/100 milliliters solution)

G = a constant

N = the total number of chambers

n = the n^{th} consecutively numbered chamber

C_o = initial or average solute concentration of solution to be purified (grams solute /100 milliliters solution)

f_p fraction of zone volume transferred each cycle in one compartment of the refiner product stream (dimensionless)

*Pfann, pages 141-5. (Reference 3).

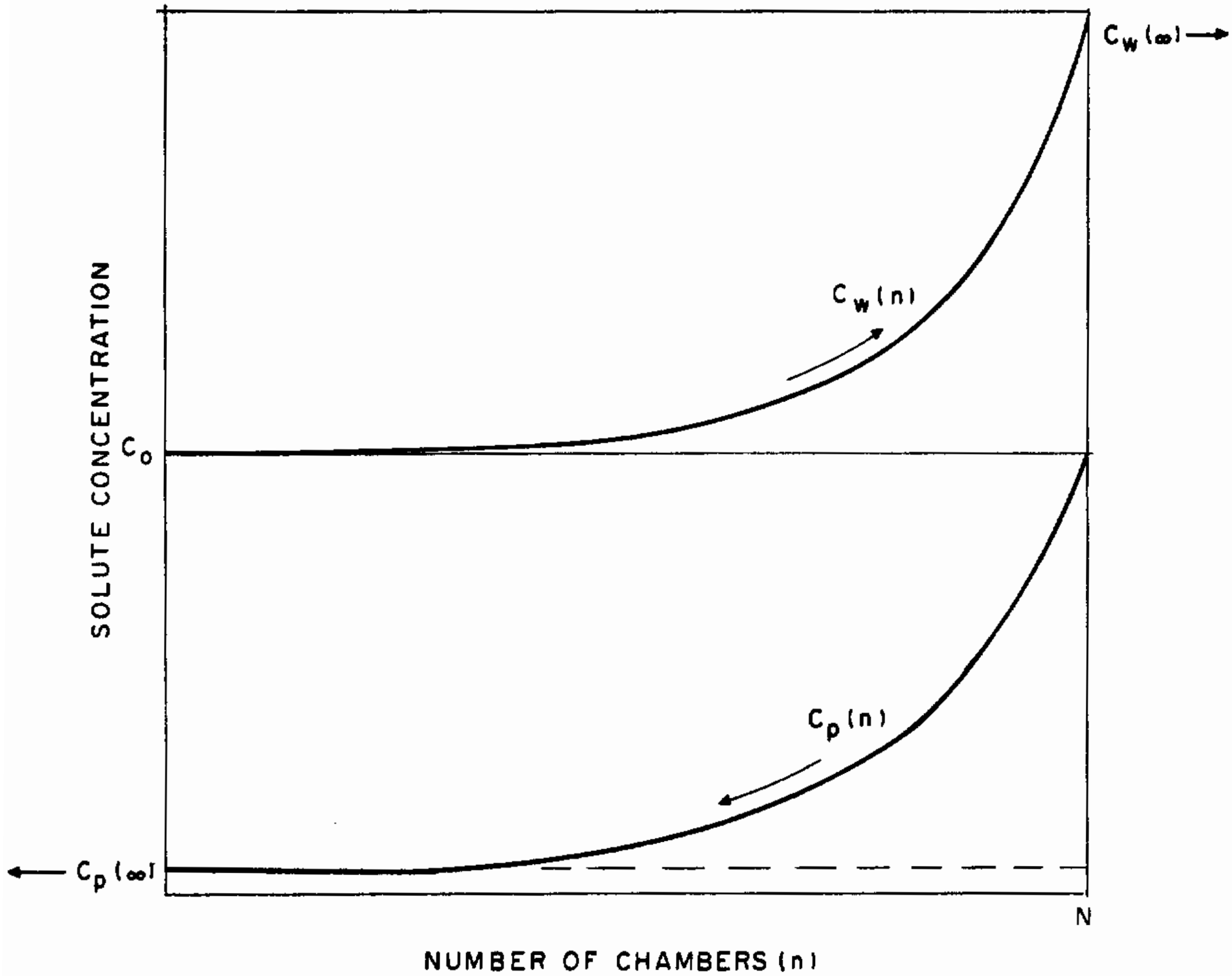


Figure 5. Solute Distribution in Cross-Flow Zone Refiner

The solute concentration distribution in the waste stream is given by:

$$\frac{C_{w(n)}}{C_o} = 1 + \frac{f_p}{f_w}\left(1 - G^n - \frac{C_{p(\infty)}}{C_o}\right) \tag{11}$$

where

$C_{w(n)}$ = solute concentration in the waste stream in compartment n (grams solute/100 milliliters of solution)

f_w = fraction of zone volume transferred each cycle in one compartment of the refiner product stream (dimensionless)

The values $C_{p(\infty)}$ and $C_{w(\infty)}$ are readily derived from the equations of zone refining with an infinite number of passes [Reference Equations (7) and (8)].

Three qualitative approaches have been presented which, together with the experimental data, offer a means of estimating the energy requirements and efficiency of engineering schemes.

SECTION II
EXPERIMENTAL PROGRAM

EXPERIMENTAL PROCEDURE

Calculations were made to determine the requirements of the experimental apparatus. It was decided to investigate freezing rates initially in the range from 10^{-3} to 5×10^{-5} cm/sec. The apparatus had to be constructed to permit investigation of the effects of stirring, gravity, and freezing rates. These requirements were met by a device providing constant but adjustable heat flow from the freezing charge to a cold bath.

The amount of liquid frozen in any one run was between 50 and 100 cubic centimeters. The maximum charge thickness was 5 centimeters. These two limitations resulted in a charge diameter of approximately 5 centimeters. The temperature differential across one centimeter of ice, at various freezing rates, is given by the equation:

$$\frac{\Delta T}{L} = \frac{\Delta H_f \rho}{\gamma} f \qquad (12)$$

where

ΔT = temperature differential (°C)

ΔH_f = heat of fusion (cal/gm)

L = length of frozen charge along axis of freezing (cm)

ρ = density (gm/cm^3)

γ = thermal conductivity of ice (cal/°C cm sec)

For the system under consideration, ΔH_f is approximately 80 cal/gm, ρ is approximately 1 gm/cm^3, and γ is approximately 0.0006 cal/°C cm sec.

Table 1 lists the temperature differential across one centimeter of ice for various freezing rates in the desired range. The maximum temperature differential which must be maintained from the cold bath to the freezing interface of the sample equals the temperature gradient, multiplied by the maximum thickness of the ice (5 centimeters), plus the temperature drop across the interposed insulation. The latter temperature differential is held constant by means of an imbedded electrical heater so as to provide the desired constant rate of heat flow, and thereby a constant freezing rate.

Table 1. Temperature Differential Across 1 Centimeter of Ice for Various Freezing Rates

Freezing Rate (f) (cm/sec)	Temperature Differential (°C/cm)
10^{-3}	13
5×10^{-4}	6.6
10^{-4}	1.3
5×10^{-5}	0.66

The design of the experimental apparatus was based on the considerations presented above. The physical configuration is described in Figure 6. Two devices were made, each containing a different control-element insulator across which the constant temperature differential was to be maintained. The apparatus having the higher thermal-conductivity insulator (0.005 cal/°C cm sec) was used for freezing experiments with freezing rates above 10^{-4} cm/sec. The other apparatus contained an insulator having a thermal conductivity of 0.0004 cal/°C cm sec and was used for experiments with freezing rates below 10^{-4} cm/sec.

The heaters are flat helical coils of varnish-insulated nichrome wire. The resistance of each heater is 37 ohms.

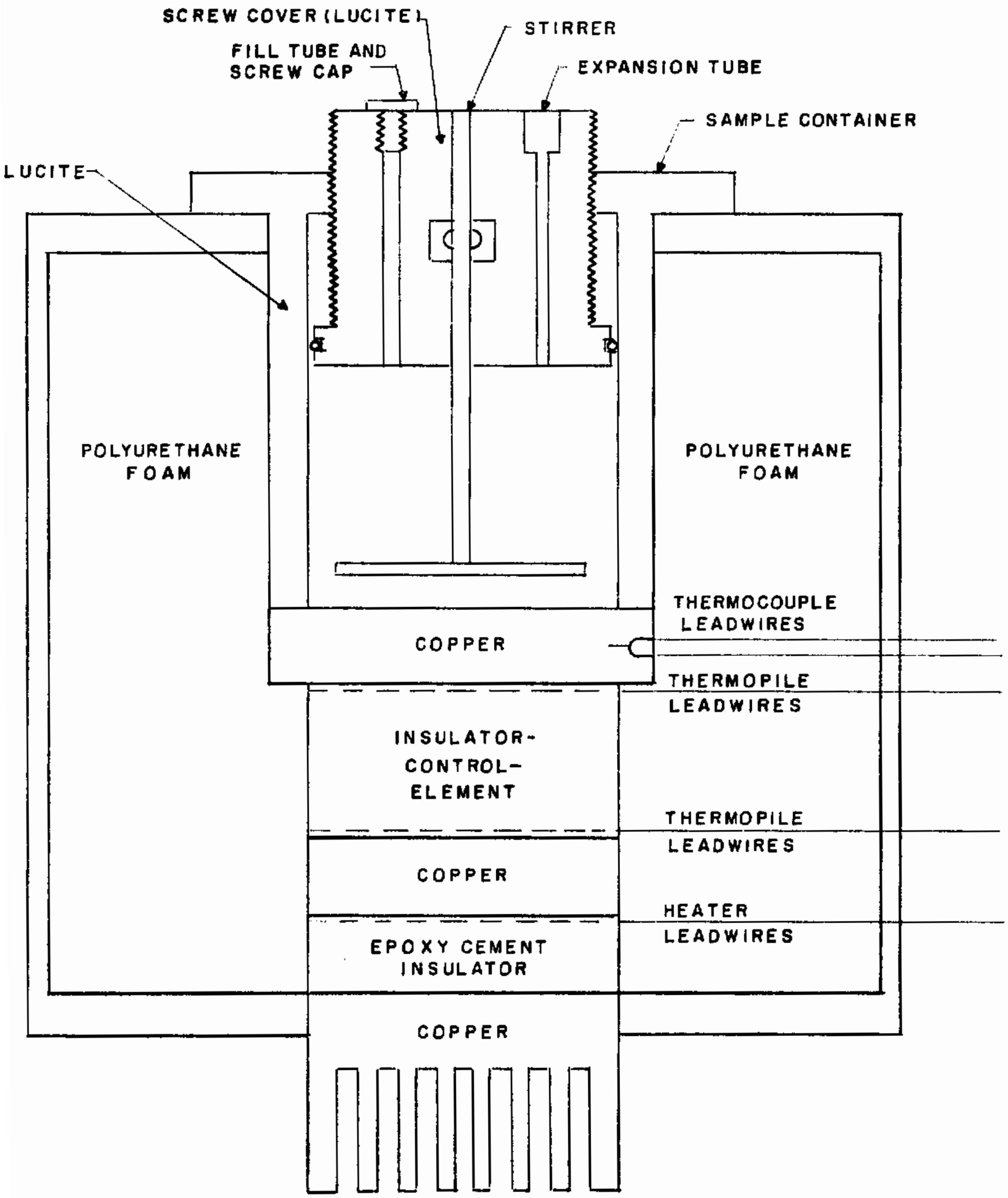


Figure 6. Freezing Apparatus

The temperature sensors in each apparatus consist of a copper-constantan thermopile. Copper tap wires at various points of the thermopile provide suitable potential outputs for temperature differentials of 5 to 60°C across the insulator control element. The output of the sensors control the heater as shown in Figure 7 by means of a cam attached to the motor of a temperature recorder. A copper-constantan thermocouple is embedded into the copper plate at the bottom of the sample container. The output of this thermocouple is used to monitor the temperature at the bottom of the sample chamber using a Brown Temperature Indicating Potentiometer. The measured temperature was used to determine the time when freezing started and thereby to establish a check on the freezing rate.

For experiments involving agitation, the freezing chamber of each apparatus was modified by drilling a hole in the center of the screw cover, fitting the hole with an O-ring, and inserting the stirrer shaft. The stirrers were constructed as shown in Figure 8. The second type of stirrer was found to be superior to the first and was put into use after the initial experiments involving agitation had been completed. Two 40-rpm, 60-cps synchronous motors were used to drive the stirrers. Figure 9 shows the freezing apparatus set up for a freezing experiment with agitation.

For freezing experiments involving a reversal of the usual freezing direction (i.e., of the direction of gravity with respect to the freezing direction), the heat exchanger end of the freezing apparatus was fitted with an aluminum container, the expansion hole in the screw cover was fitted with a U-shaped glass expansion tube, and the entire apparatus was turned upside down.

PROCEDURE FOR FREEZING EXPERIMENTS

A piece of aluminum foil was applied with silicone grease to the copper surface at the bottom of the freezing chamber. With the screw cover in place, the lucite sample container was assembled to the freezing chamber. Approximately

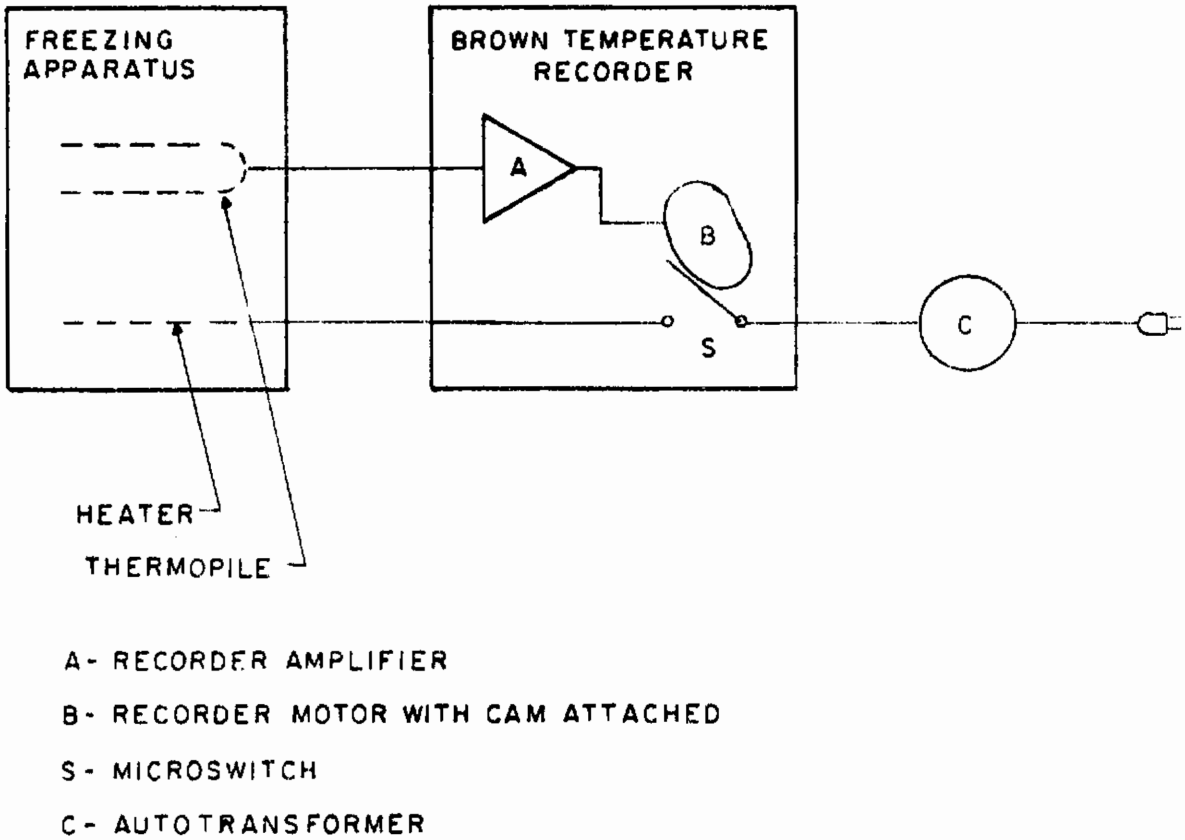


Figure 7. Diagram of Temperature Control System for Freezing Apparatus

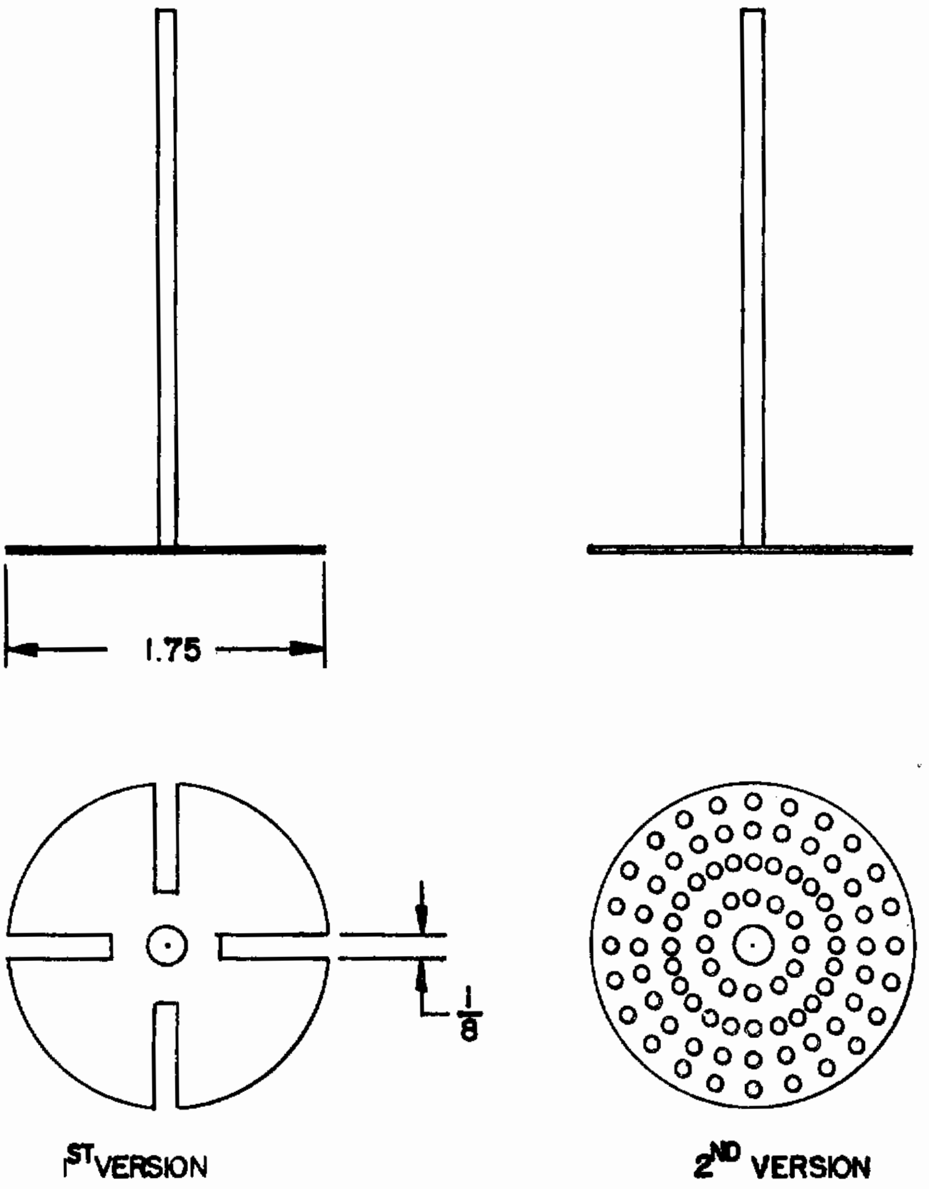


Figure 8 Stirring Discs

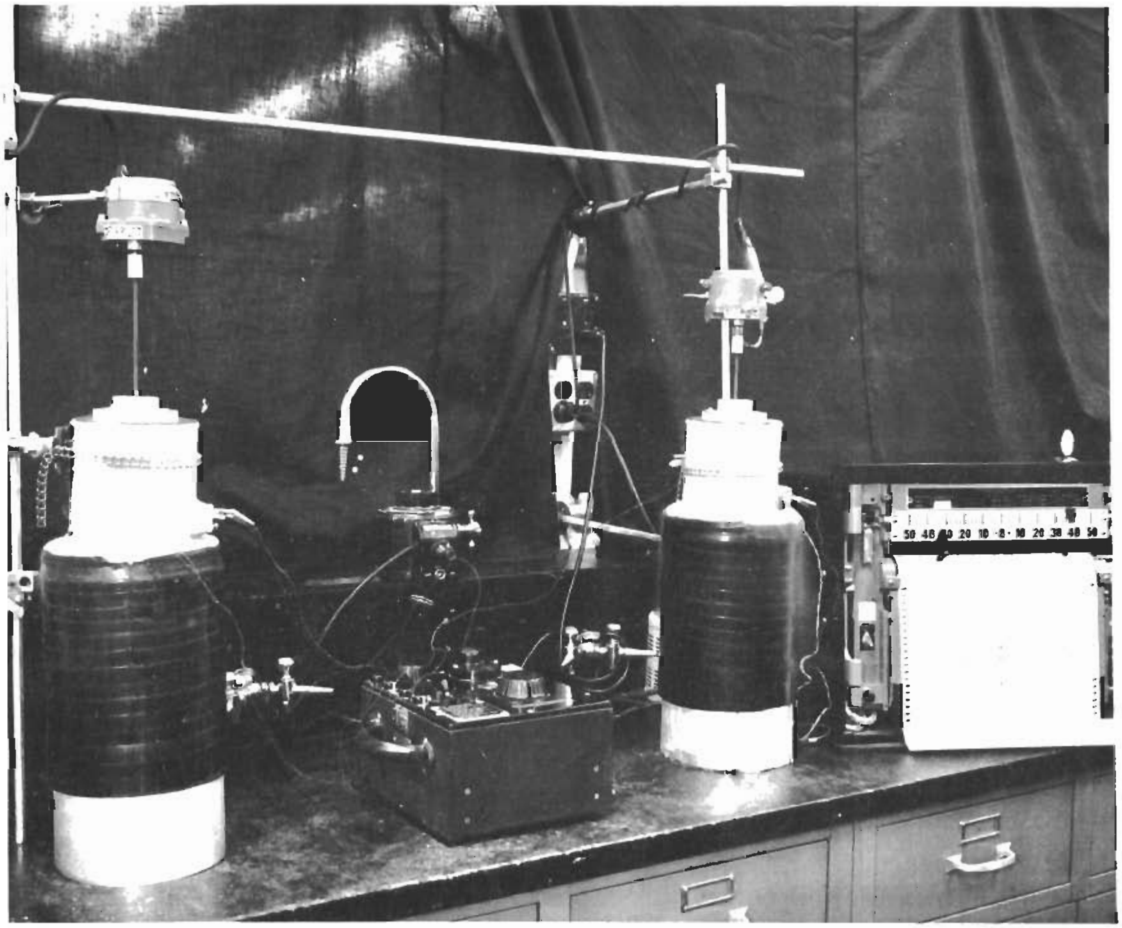


Figure 9. Freezing Apparatus for Slow and for Fast Freezing, Set Up for Experiments with Agitation in the Usual Freezing Direction

60 cm^3 of the solution was pipetted into the freezing chamber through the fill hole in the screw cover. The copper heat exchanger at the bottom of the apparatus was immersed in the coolant contained in a Dewar flask. The junctions in the thermopile control element which gave the desired output voltage were connected to the recorder. The control cam was set to turn the heater switch off and on at the desired voltage. Approximately 35 volts were applied to the heater circuit. The temperature in the copper plate at the bottom of the freezing chamber was monitored by means of a thermocouple to determine when freezing temperatures were first reached. The freezing rate was measured by means of a dip stick inserted through the expansion hole of the screw cover and resting against the freezing interface. The over-all freezing rate was also measured by determining the thickness of the frozen charge at the end of each freezing run and dividing by the total freezing time.

The procedure used for freezing experiments with agitation was essentially the same as that for experiments without agitation except that the distance of the stirrer from the interface was maintained manually at approximately 1/16 inch. For experiments involving a reversal of the freezing direction, the aluminum foil and sample container were assembled as previously described. Approximately 60 cm^3 of sample were introduced through the fill hole in the screw cover. The screw cover was turned down until no entrapped air remained and a small amount of the solution had leaked out of the expansion hole and the fill hole. The screw cap was then assembled to the fill hole and tightened. A U-shaped glass expansion tube was inserted into the expansion hole of the screw cover and the entire freezing apparatus was turned upside down. An aluminum cup was assembled to the heat exchanger end of the freezing apparatus (now the top of the apparatus). The aluminum can was filled with coolant, and an inverted Dewar flask was placed over the entire assembly. Freezing rates and the position of the stirrer were controlled as previously described.

SECTIONING

Several methods of sectioning the frozen charge were tried. The initial apparatus for sectioning consisted of an electrically heated nichrome wire under tension. The use of this apparatus, however, proved tedious and slow, and resulted in considerable weight loss due to melting. Subsequent sectioning was performed on a small band saw whose blade had previously been thoroughly cleaned (see Figure 10).

Initially the frozen charges were cut into three sections; after adaptation of the band saw, the frozen charges were cut into five sections. The total weight of the frozen charge was determined before sectioning. After sectioning, the weight of each slice was determined. The total amount of weight lost as a result of slicing was approximately 10 per cent of the total charge weight. Since the frozen charges were uniformly cylindrical and the density of the frozen charge was relatively uniform, the weight fraction of each slice was approximately equal to the volume fraction frozen along the cylindrical axis. It was observed that, for freezing experiments with both urine-equivalent solutions* and urine, a super-cooled layer of liquid forming at the surface of the cooling plate caused very rapid freezing of the first one or two millimeters of charge, thereby increasing the concentration of the first fraction. This condition was subsequently eliminated by the addition of very fine, white beach sand (less than 140-micron diameter) to the liquid samples. The sand was filtered out of the urine after sectioning and melting of the fractions. In general it was considered good practice to filter the fractions of the frozen charge in order to remove sand and any particles of dirt resulting from the slicing.

SOLUTIONS AND ANALYTICAL PROCEDURES

The solutions used for preliminary freezing experiments with and without agitation, and with reversal of the usual freezing direction, were 8, 4, 1.6,

*Two per cent urea and two per cent sodium chloride solution.

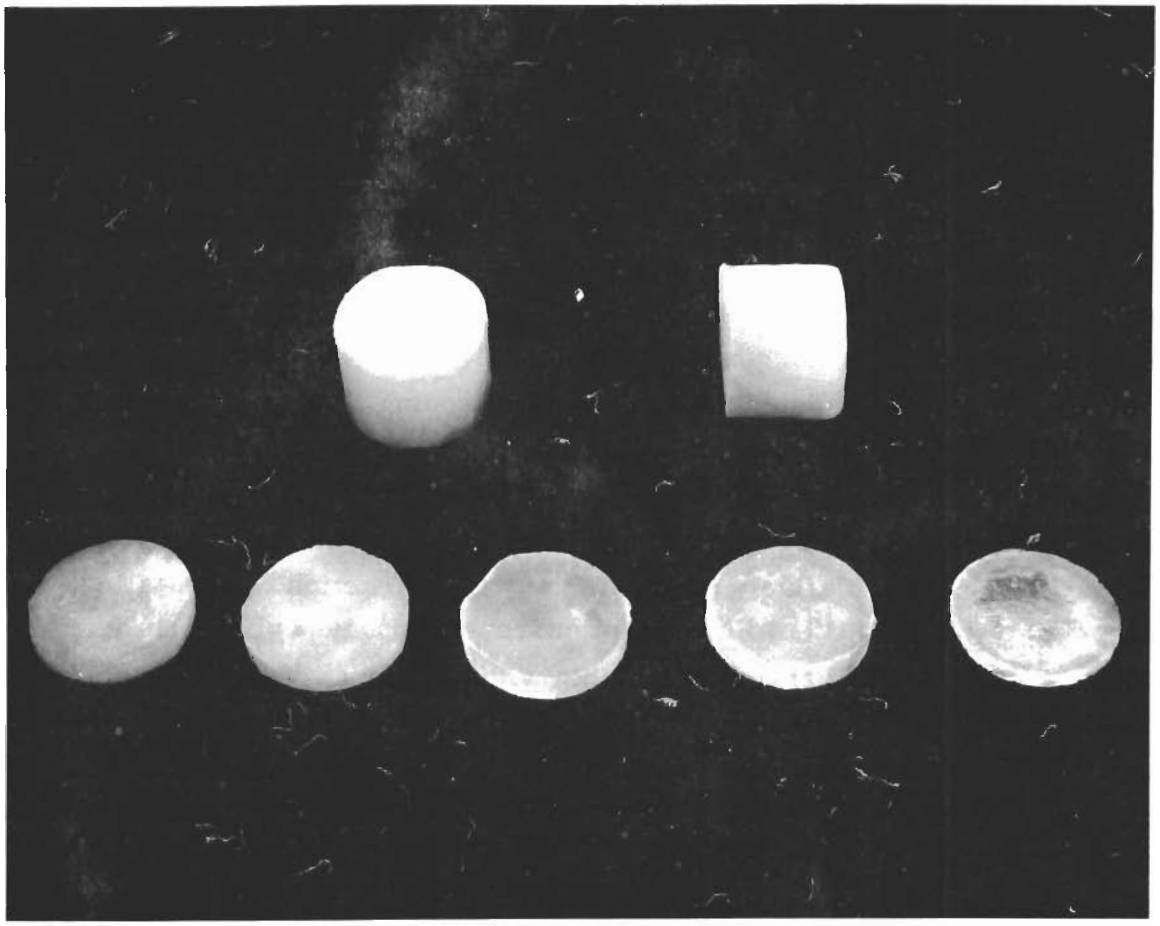


Figure 10. Frozen Charges of Urine-Equivalent Solution, Before and After Slicing

and 1 per cent sodium chloride solutions and 10, 5, 2, and 1 per cent urea solutions. In addition, a solution of urine-equivalent concentrations of urea and sodium chloride (2 per cent urea and 2 per cent sodium chloride) was prepared and subjected to freezing experiments with agitation and with reversal of the usual freezing direction.

The procedure for determining the concentration of sodium chloride solutions consisted of pipetting a known volume of the solution into a crucible and evaporating this sample at 200°F for approximately five hours. The concentration of the urea solutions was determined by evaporation of a known volume of solutions for a period of five hours at 150°F. Evaporation of the urea solutions above that temperature resulted in decomposition of the urea, thereby causing error in determining the concentration.

For urine-equivalent mixtures of sodium chloride and urea, a known volume of solution was first evaporated for a period of 5 hours at 150°F, giving the total solids concentration of the solution. Subsequently, the solution was fired at 1250°F, causing decomposition of the urea and leaving the sodium chloride The urea concentration was determined by the difference between the total solids concentration and the sodium chloride concentration.

The urine used for these freezing experiments was collected from seven white males between the ages of 25 and 35 and intermixed to give a total of approximately one gallon. This amount was sufficient for all subsequent freezing experiments, thus providing a standard urine of constant concentration. After the urine was pre-mixed in a one-gallon jug, it was poured off into a number of 100-ml containers. The urine was kept refrigerated at all times. Refrigeration caused the formation of a white precipitate, believed to be primarily uric acid, which constituted approximately 0.1 per cent of the total solids concentration. (The white precipitate redissolved when the urine was brought back to room temperature.) The white precipitate was filtered out of the urine samples prior to every freezing experiment.

For several freezing experiments the urine was diluted with distilled water to 50, 25, and 10 per cent of its initial total solids concentration. The total solids concentration of urine and of the diluted urine solutions was determined by evaporation at 150°F in the same manner as urine-equivalent solutions. The total mineral concentration was determined by firing the evaporated samples at 1250°F. For urine dilutions of 25 and 10 per cent, the above method of total mineral determination was found to be inaccurate because of the low weights involved. It was found that the total mineral concentration corresponded within 95 per cent to the total sodium chloride concentration, determined by precipitation of the chloride with silver ion; it was therefore possible, for dilute solutions, (10 and 25 per cent urine) to determine the total mineral concentration in terms of the sodium chloride concentration by titration with a known concentration of silver nitrate and subsequent back-titration with potassium thiocyan~~ide~~ate in the presence of ferric ion.

The ionic concentration of urine and of diluted urine was determined by measuring the conductivity of 100:1 dilutions in distilled water. The conductivity measurements were made on an Industrial Instruments Company Model RC16 conductivity bridge at 60 cps. (No change of polarization was observed upon checking the conductivity at 1000 cps.) A standard conductivity cell with platinum black electrodes was used in conjunction with the conductivity bridge. The electric conductivity of various dilutions of the original urine was measured (see Figure 11). Slices from the frozen charges, diluted to 0.01 of their original concentration, were given conductivity tests. By comparing the measured conductivity of these fractions with the conductivity curves, the dilution or concentration of ionic species in the slices with respect to the original urine was determined.

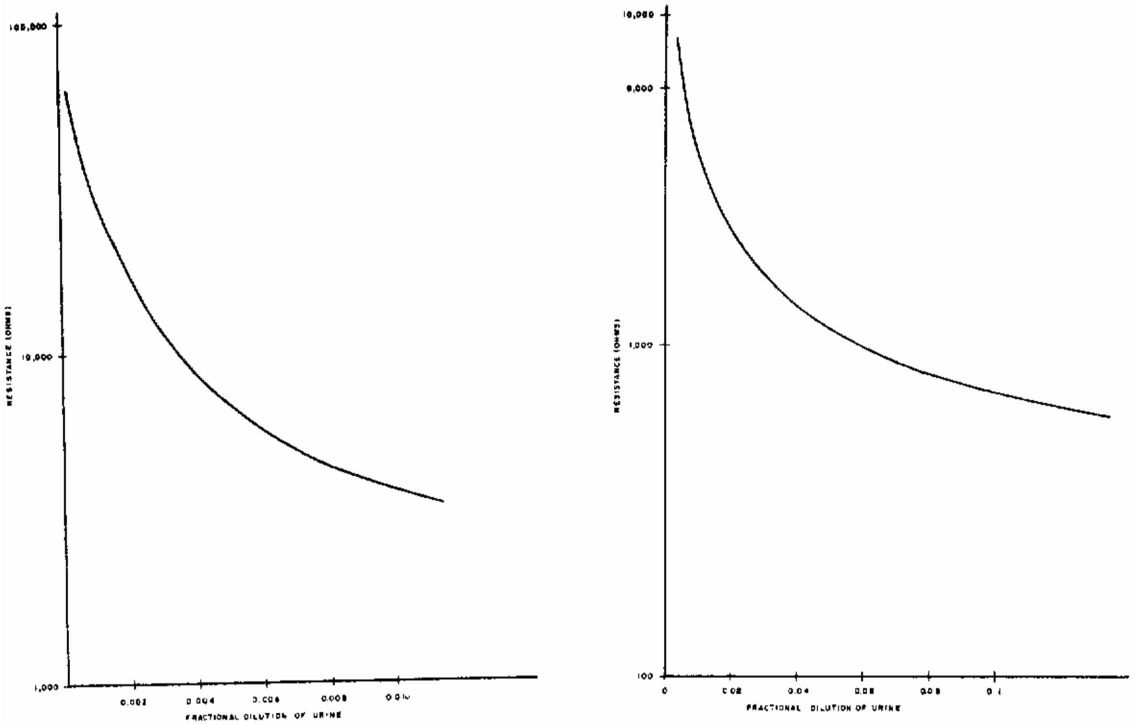


Figure 11. Fraction of Urine versus Resistance (Cell Constant = 0. 1)

SECTION III
EXPERIMENTAL RESULTS

Freezing experiments without agitation were performed on sodium chloride solutions (concentrations of 4, 1.6, and 1 per cent) and on urea solutions (concentrations of 10, 5, 2, and 1 per cent). The freezing rates used for these experiments were in the range from 7×10^{-4} to 5×10^{-5} centimeters per second. The results of these experiments are tabulated in Table 2.

Table 2. Distribution Coefficients for Freezing Experiments without Agitation (Sodium Chloride Solutions and Urea Solutions)(±15 per cent)*

Solute	Initial Concentration(C_0) (gms/100 ml)	Freezing Rate, (f) 10^{-5} (cm/sec)	Distribution Coefficient Effective (k_1)	Distribution Coefficient Equilibrium (k_0)**	δ/D** (sec/cm)
Sodium Chloride	4.0	5 20	0.80 (0.74)	0.77	
	1.6	5 70	0.82 0.94	0.80	2100
	1.0	5 70	0.82 0.96	0.80	2600
Urea	10.0	5 50	0.82 0.95	0.81	3200
	5.0	5 50	0.72 0.90	0.70	3800
	2.0	5 50	0.60 0.73	0.59	1300
	1.0	50	0.72		

*Indicates confidence factor in terms of per cent error.

**The δ/D and k_0 values are each computed from two or more freezing rates, by the method described in Section I.

The equilibrium distribution coefficients and δ/D values obtained for these experiments were computed by means of Equation (4). Since this equation is based upon the assumption that the liquid phase is agitated, the values of the equilibrium distribution coefficient obtained for these experiments without agitation are considerably different from those obtained with agitation. Table 3 lists the values of the effective and the equilibrium distribution coefficients for agitated freezing experiments involving the same solutions. Comparison of Tables 2 and 3 indicates the great difference, particularly in the values of the effective and the equilibrium distribution coefficients, between agitated and nonagitated freezing experiments.

Table 3. Distribution Coefficients for Freezing Experiments with Agitation (Sodium Chloride Solutions and Urea Solutions)(±10 per cent)

Solute	Initial Concentration (C_o) (gms/100 ml)	Freezing Rate(f) (10^{-4} cm/sec)	Distribution Coefficient		δ/D (sec/cm)
			Effective (k_1)	Equilibrium (k_o)	
Sodium Chloride	8.0	2.0	0.64		
	4.0	2.0 3.0 5.0	0.47 0.50 0.57	0.38	1300
	2.0	7.0	0.46		
	1.6	2.0 5.0	0.36 0.55	0.24	2600
	1.0	2.0	0.32		
Urea	10.0	1.5	0.44		
	5.0	1.5 5.0	0.46 0.54	0.42	900
	2.0	1.5 5.0	0.41 0.49	0.38	1000
	1.0	1.5 5.0	0.34 0.49	0.29	1300

The data from agitated freezing experiments with sodium chloride solutions and urea solutions show a variation of both the effective and equilibrium distribution coefficients as a function of the initial concentration of the solutions. This variation is plotted for sodium chloride in Figure 12(b) and for urea in Figure 12(c). Though the value of both the effective and the equilibrium

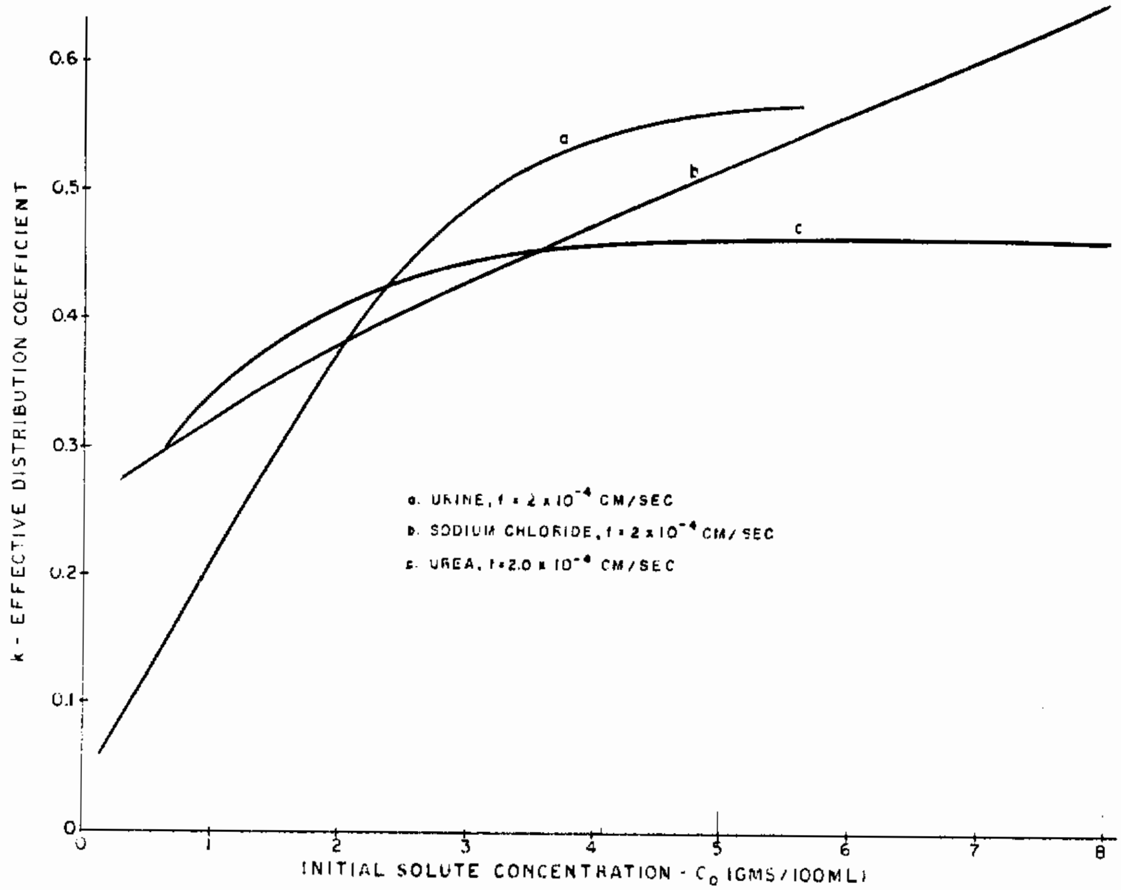


Figure 12. Dependence of the Effective Distribution Coefficient Upon Initial Solute Concentration Using Agitated Freezing

distribution coefficients decrease with decreasing concentration, the deviation of the system from equilibrium changes in the opposite direction; that is, the ratio of the effective distribution coefficient with respect to the equilibrium coefficient increases with decreasing concentration. This relationship is shown in Figure 13.

The results of freezing experiments involving an agitated urine-equivalent solution, urine, and diluted urine are given in Table 4.

Table 4. Distribution Coefficients for Freezing Experiments with Agitation (Urine-Equivalent Solution, Urine, and Diluted Urine)(±10 per cent)

Solute	Initial Concentration (C_0) (gms/100 ml)	Freezing Rate (f) (10^{-4} cm/sec)	Distribution Coefficient Effective (k_1)	Distribution Coefficient Equilibrium (k_0)	δ/D (sec/cm)
Urine Equivalent*	4.0	2.0	0.59		
Urine	4.9	2.0 7.0	0.56 0.67	0.51	940
Diluted Urine	2.45	2.0 7.0	0.44 0.60	0.38	1300
	1.22	2.0 7.0	0.24 0.43	0.16	1700
	0.49	2.0 7.0	0.12 0.30	0.06	2300

*Urine-equivalent solution contains 2 per cent sodium chloride and 2 per cent urea.

It will be noted in Table 4 that the effective and the equilibrium distribution coefficients are directly proportional to the initial solids concentration (as in the case of urea and of sodium chloride solution) and that the deviation from equilibrium expressed in terms of the ratio of the effective distribution coefficient to the equilibrium coefficient is inversely proportional to the initial solids concentration. Figure 12(a) shows the variation of the distribution coefficient with initial solute concentration for urine, and Figure 13(a) shows the deviation from equilibrium (k/k_0) with initial solute concentration for urine.

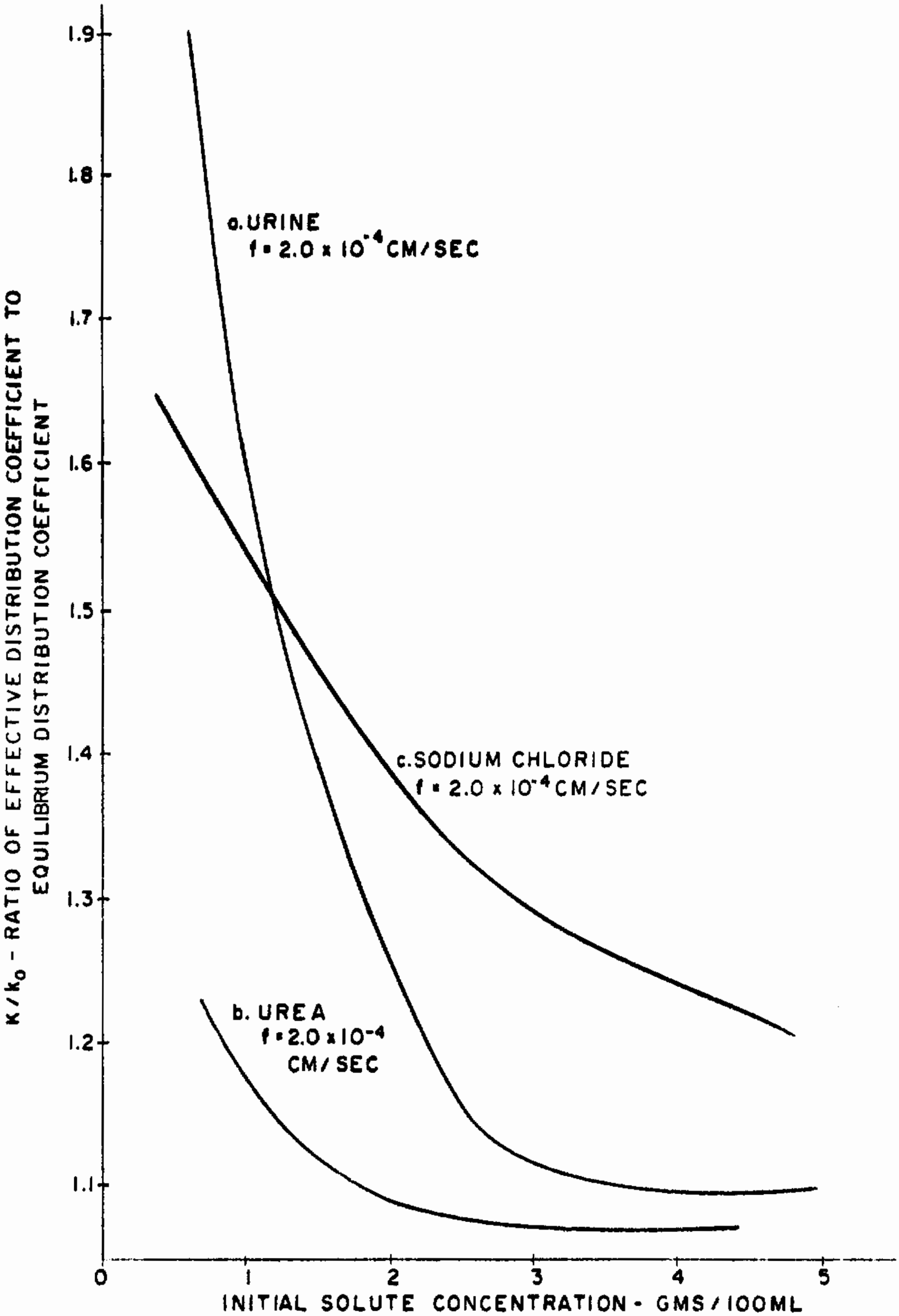


Figure 13. Ratio of Effective Distribution Coefficient to the Equilibrium Distribution Coefficient versus Initial Solute Concentration

The relationship between the deviation from equilibrium (k/k_o) and the solids concentration for sodium chloride solutions, urea solutions, and urine leads to the conclusion that as the solids concentration in the liquid decreases, the thickness of the diffusion layer (δ), might increase. It must also be appreciated that as k and k_o get small, an absolute difference in k makes the ratio larger. This condition might be alleviated by increasing the stirring efficiency in solutions in the lower concentration range.

Freezing experiments with a reversal of the direction of freezing were performed on 2 per cent urea solutions, urine-equivalent solutions, and urine. All freezing experiments involving the reversal of usual direction of freezing were run at a freezing rate of 2×10^{-4} centimeters per second. The values of the effective distribution coefficient obtained with the reversal of the usual freezing direction are given in Table 5.

Table 5. Effective Distribution Coefficients for Freezing Experiments with the Usual Freezing Direction and the Reversed Freezing Direction

Solution	Solids Concentration (C_o) (gms/100 ml)	Distribution Coefficient	
		Normal Freezing Direction (k_1)	Reversed Freezing Direction (k_1)
Urea	2.0	0.41	0.40
Urine Equivalent	4.0	0.59	0.55
Urine	4.9	0.56	0.57

Freezing experiments involving a reversal of the normal direction of freezing did not appreciably change the distribution coefficients. Because of the more tedious experimental procedure for freezing experiments in the upside-down configuration, the small gain in distribution coefficient, if real, was not considered sufficient to warrant further experiments with this parameter.

As in the freezing experiments with urine and diluted urine, the distribution of ionic species (obtained by conductivity measurements) and the distribution of total mineral concentration (obtained by firing at 1250°F) agreed with the distribution of the total solids concentration within 5 per cent. This leads to the conclusion that both the ionic and nonionic constituents of urine are distributed in much the same manner. Therefore, the effective distribution coefficient for total solids is used to characterize the over-all separation obtained. It should be pointed out, however, that some trace elements in urine may have a distribution coefficient considerably different from the over-all average obtained in these experiments. However, the physiological effects of solutes of urine in trace quantities are negligible.

In general, it can be concluded that:

1. Agitation is necessary in order to obtain low distribution coefficients with the solutions observed in these experiments.
2. For solute concentrations above 1 per cent, the conditions of agitation provided in these experiments result in distribution coefficients close to equilibrium.
3. Reversal of the direction of the gravitational field with respect to the direction of freezing has a relatively small effect upon the effective distribution coefficient.
4. Both ionic and nonionic constituents of urine are distributed with approximately equal efficiency.

The relationship between the effective distribution coefficients and the initial concentration yields information concerning the energy requirements of the various freezing schemes (see Section V).

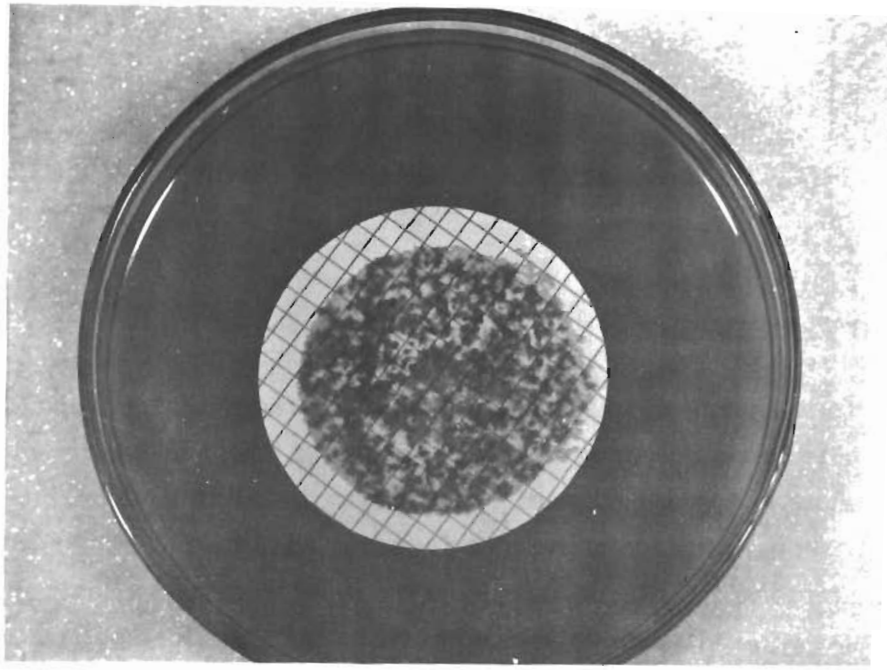
SECTION IV
BEHAVIOR OF MICRO-ORGANISMS UNDER FREEZING CONDITIONS

EXPERIMENTAL PROCEDURE

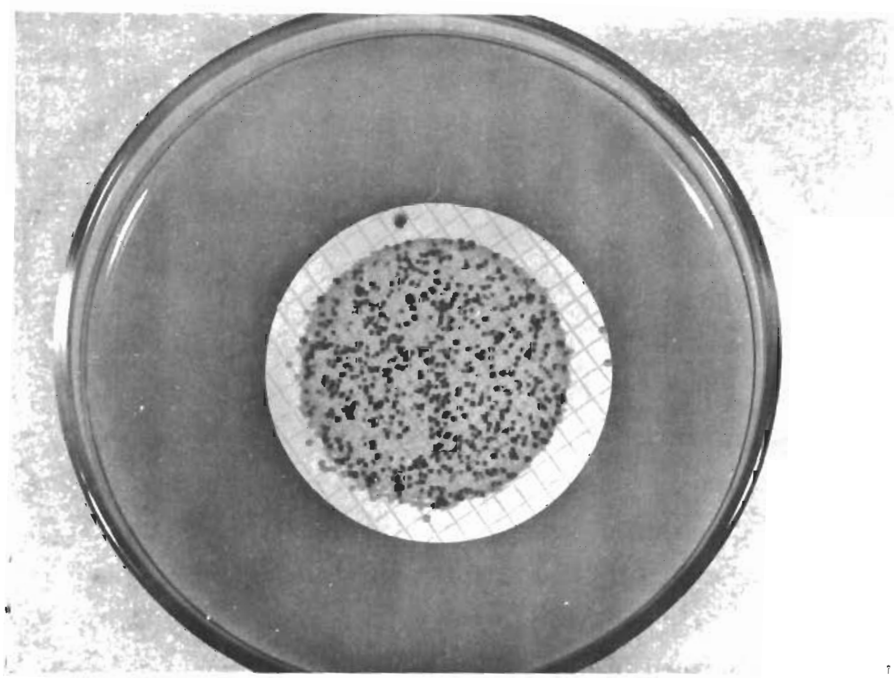
One hundred milliliters of urine were contaminated with 1 ml of a 1/1000 dilution of an 18- to 24-hour-old broth culture of Serratia Marscessens. The freezing apparatus was sterilized, and approximately 60 ml of the contaminated urine were frozen, with agitation at a freezing rate of 2×10^{-4} centimeters per second as described in Section II. This freezing rate was chosen because it is likely to be used in actual practice. Beach sand was added to the urine in order to facilitate nucleation. The frozen charge was sectioned into five slices on a sterilized band saw. The slices were delivered, in the frozen condition, to Dr. V. W. Green, consultant bacteriologist. The slices were allowed to melt slowly to a temperature of 3°C in a water bath. Aliquots of the melted urine (1, 2, and 10 ml amounts) were passed through membrane filters (Millipore size DA). The filters were incubated for a period of 24 hours at 35°C in a tryptone-glucose-yeast-extract agar. The above procedure was chosen after some experimentation.

EXPERIMENTAL RESULTS

The Serratia Marscessens micro-organisms were distributed in such a manner that the last slice to freeze (constituting approximately 20 per cent of the total charge) contained in the range of 3 to 4 times as many bacteria per unit volume as the remaining four, which had approximately equal concentrations of bacteria. The relative distribution is shown in Figure 14. In addition to the bacteria with which the urine was inoculated, there appeared a strain of bacteria of unknown nature, apparently introduced by the white sand used to provide nucleation. This strain of bacteria also distributed itself in such a manner that the last slice contained the highest number of bacteria. Due to some unknown percentage of bacteria killed in the process of freezing, and due to the possibility ofclustering phenomenon, it is not meaningful to attempt to sum the bacteria of all sections in order to obtain the initial concentration.



a. From Last Slice to Freeze



b. From First Slice to Freeze

Figure 14. Serratia Marscessens Cultures

SECTION V

ENGINEERING CONSIDERATIONS

The feasibility of reiterative freezing for recovering potable water from urine is conveniently expressed in terms of the energy required to obtain a given yield of potable water from the initial urine. This energy is only that which is required to freeze urine and solutions of intermediate concentrations in the process of refining. It does not include the energy requirements arising from the mechanical configuration of the recovery system, or from special environmental conditions in which the system is to operate.

In Section III it was pointed out that the effective distribution coefficient of urine varied with the initial solute concentration. The equations given for the various freezing schemes discussed in Section I of this report are applicable in situations where the distribution coefficient is independent of initial concentration. It is therefore convenient to determine the energy requirements of at least one recovery scheme directly from the experimental data and then to find an average, effective distribution coefficient which does not vary with concentration, but which yields energy requirements identical with those obtained from the experimental results.

Figure 15 is a plot of the fraction of the initial solute concentration versus per cent of charge frozen for various initial concentrations of urine. Figure 16 is a diagramatic representation involving "normal" freezing as described in Section I. The scheme involves partial freezing of each charge until a given fraction (80 per cent in Figure 16) of the charge is frozen and a liquid concentrate remains. The concentrates are recombined and are recycled into the freezing process at concentrations encountered in the freezing steps of the process.

Such an analysis shows that in order to attain 700 ml of water containing a solids concentration of 400 parts per million out of one liter of urine, it is necessary to freeze the equivalent of 9200 ml of liquid. Defining the number of equivalent

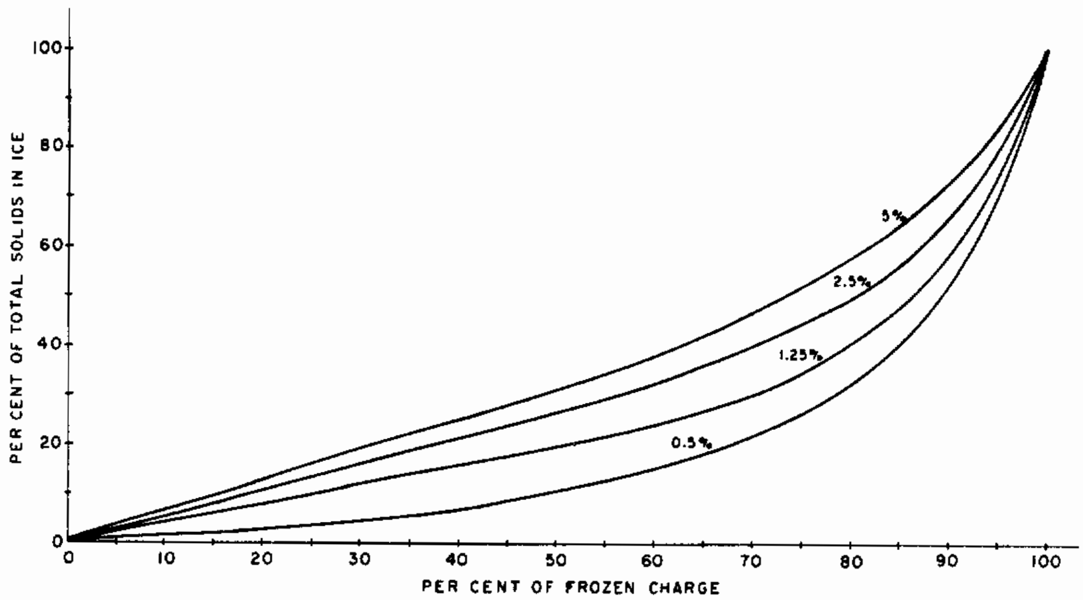


Figure 15. Per Cent of Total Solids versus Per Cent of Frozen Charge for Several Initial Total Solid Concentrations of Urine

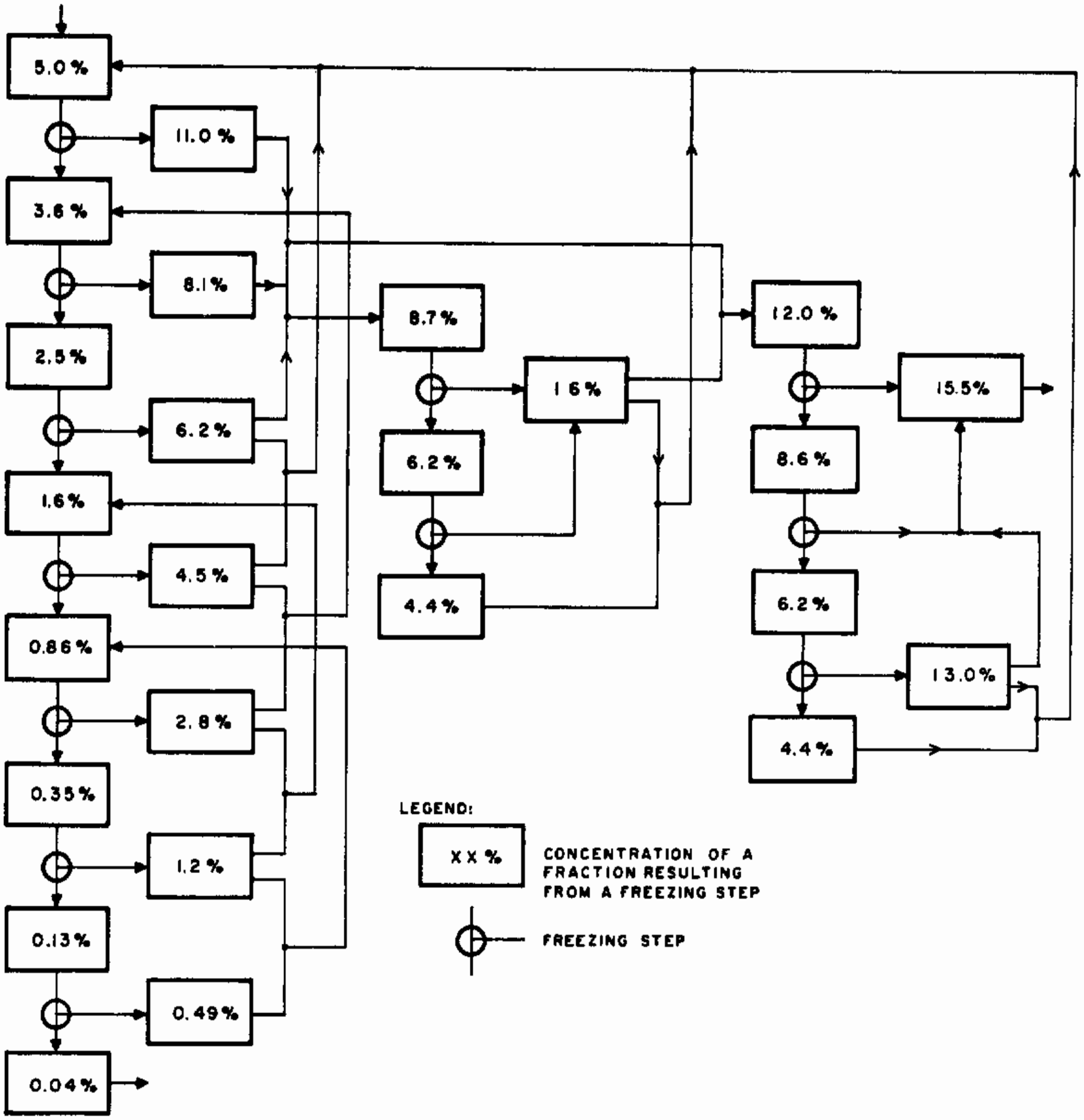


Figure 16. Diagram of a Reiterative Freezing Scheme (80 per cent frozen each step)

cycles as the number of milliliters of liquid that must be frozen in order to recover one milliliter of potable water containing less than 500 parts per million of impurity, the above figure corresponds to 13.1 equivalent cycles. It was found that the number of equivalent cycles was a function of the yield and was relatively independent of the fraction recovered in each freezing step (at least for fractions between 60 and 80 per cent). Figure 17(a) is a plot of the required number of equivalent cycles versus attainable yield for this type of recovery scheme.

Equation (1) may be used to obtain the theoretical average fraction of initial concentration as a function of the fraction frozen in the following manner:

$$\frac{\overline{C}_s}{C_o} = \overline{P} = \frac{k\int_0^g (1-g)^{k-1}\,dg}{\int_0^g dg} = \frac{-(1-g)^k + 1}{g} \qquad (13)$$

Furthermore, the fraction of total solids in the ice as a function of that fraction (as it was plotted for experimental data in Figure 15) is:

$$\overline{P}g = 1 - (1-g)^k \qquad (14)$$

Equation (14) applies to values of the effective distribution coefficient which do not vary with initial concentration. Having derived an equation for a theoretical distribution that has the same coordinates as those of Figure 1, the "normal" freezing schemes, with 70 per cent recovery in each step of the process, were determined for several values of the effective distribution coefficient between 0.2 and 0.4. The energy values (expressed as the number of equivalent cycles) obtained from calculation of these freezing schemes were used to determine that value of the theoretical effective distribution coefficient which yielded the same energy requirements obtained from the experiments. The value of this theoretically-derived average distribution coefficient was found to be 0.26.

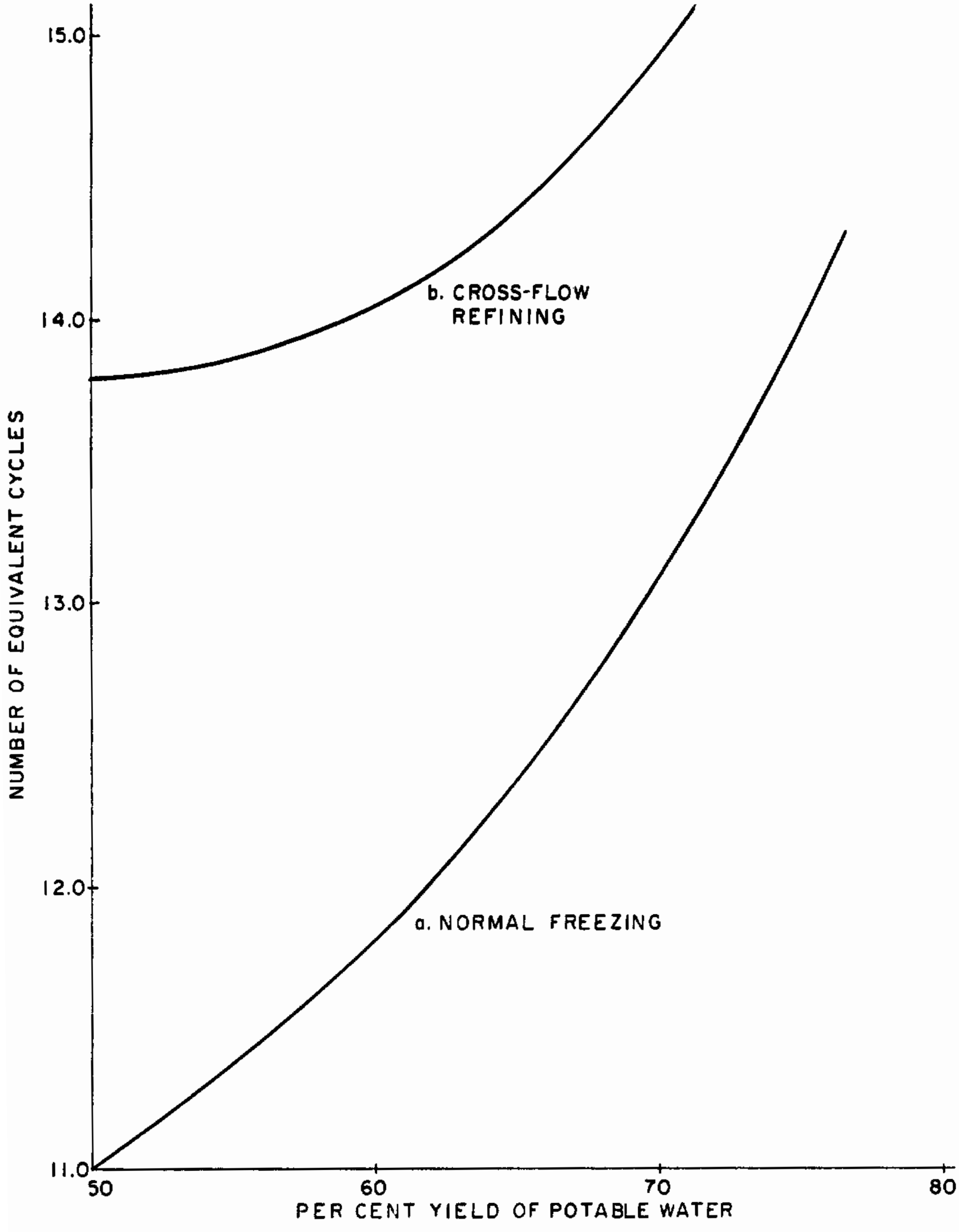


Figure 17. Number of Equivalent Cycles versus Per Cent Yield of Water Recovered from Urine

Having thus obtained a value for the average effective distribution coefficient of urine, it is possible to determine the parameters for a cross-flow zone refiner as described in Section I. Using Equations (7) through (11), it was found that for an average effective distribution coefficient of 0.26, optimum conditions are attained when the cross-flow zone refiner is four zones long in the direction of the zone travel, and is divided into four chambers. For this refiner, with a liquid having an average effective distribution coefficient of 0.26, the number of equivalent cycles required to obtain yields from 50 to 80 per cent are plotted in Figure 17(b).

Two underlying assumptions were made in calculating these parameters:

1. When a volume of feed is introduced and an equal volume of product and/or waste is displaced at the other end of the refiner, the fractions between partitions must not mix.

2. The refiner must be allowed to run for a period of time, so that intermediate, "steady state" concentrations of the solutions contained between partitions are established.

Comparison of the requirements for normal freezing schemes with those for cross-flow zone refining shows that the number of equivalent cycles required to recover equal yields is almost identical. It is necessary to expend 80 calories to freeze one gram of water. Using this constant, the energy requirements in terms of equivalent cycles are readily converted to calories. The energy requirements calculated in this section include only that portion of the total energy which is used to freeze the urine and intermediate solutions in order to recover potable water; no allowances for energy requirements for fluid handling or heat loss through insulation are taken into consideration. On that basis, a comparison can be made between reiterative freezing and a process involving the evaporation of urine, such as distillation, based on the fact that the heat of vaporization of water is approximately 600 calories/gram, which is approximately seven times as much as the heat of fusion, assuming equal opportunities for thermal efficiency. Based upon previous experience, it is assumed that the distillation process will require from one to two cycles in order to achieve a purity of better than 500 parts per million in the product, if no extraneous recovery processes such as filtration or electrodialysis are used. This corresponds to the energy expended in approximately 15 equivalent freezing cycles, which is approximately equal to the energy requirement for a 70 per cent yield with reiterative freezing of urine. The choice between use of distillation or reiterative freezing for water recovery evidently must arise from mechanical requirements of the system design.

It is believed that phase separation of a solid-liquid phase system under zero gravity conditions is more easily achieved than phase separation of a liquid-gas phase system. On that basis, recovery systems using reiterative freezing may be more advantageous than those involving distillation.

The average water balance for a man over a 24-hour period is shown in Table 6.

Table 6. Water Cycle in Man (Reference 1)

	Input (ml)		Output (ml)
Drinking Water	1200	Urine	1400
Water in Food	1000	Feces	100
Water of Oxidation	300	Insensible water (respiration and persiration)	1000

If the food consumed contains all of the 1000 mls of water listed in the table, then the intake requirements can be easily met by recovery of the insensible water, which requires a minimum of processing, and by recovery of 14 per cent of potable water from urine; if, however, dehydrated food is used which contains anywhere from 5 to 10 per cent of water of hydration, then it becomes necessary to recover approximately 70 to 80 per cent of the urine as potable water. This maximum required yield is in the range of the energy requirements which are discussed in this section. However, judging from Figure 17, yields above 90 per cent are considered impracticable.

SECTION VI
RECOMMENDATIONS AND CONCLUSIONS

RECOMMENDATIONS FOR FUTURE WORK

It has been demonstrated in the previous section that from the point of view of the energy required to freeze the urine, reiterative freezing schemes require approximately the same energy as schemes involving the distillation of urine. These requirements are, however, only a portion of the total energy requirement for a recovery system. The remaining energy requirement is dictated primarily by the mechanical implementation of the recovery system and by the conditions under which the recovery system is to operate. Under zero gravity conditions, the separation of phases -- particularly the separation of a liquid from a vapor phase -- may be relatively difficult to achieve. The separation of a liquid phase from a solid phase or of a gas phase from a solid phase is held to require less effort than the separation of a liquid-vapor phase system. In this respect, a system using reiterative freezing may result in more economical recovery of water from urine than one involving distillation. The scope of this experimental program was limited to determining the feasibility of the reiterative freezing process as such, and the effect of various parameters such as freezing rate, the direction of gravity, agitation, and the presence of micro-organisms upon the efficiency of freezing. This feasibility having been established, questions regarding the mechanical design of the system utilizing reiterative freezing for water recovery remain to be answered. The following additional work in this field is recommended:

1. Study the requirements for phase separation of a liquid-solid and/or a solid-vapor phase system under zero gravity conditions.

2. Determine the energy requirements resulting from the mechanics of a reiterative freezing system involving, for example, the use of a pump for transporting one or both of the phases, the use of the outer void as a heat sink, and the use of solar radiation as a source of heat energy for melting, etc.

3. Determine the efficiency of filtration and other methods of sterilization as a method of removal of micro-organisms prior to zone refining.

4. Construct a prototype system based on the findings in this report and on the findings in Items 1, 2, and 3, from which the total energy requirements of an integrated recovery system can be determined.

CONCLUSIONS

This investigation has demonstrated that, in urine, a separation of solute occurs as a result of slow freezing. The degree of separation is dependent upon the rate at which freezing is allowed to proceed, upon the degree of agitation of the liquid, and upon the initial solute concentration. A reversal of the direction of gravity has little effect upon the attainable solute separation. In order to make possible a comparison of the degree to which solute separation was achieved within a frozen ingot, a parameter, called the effective distribution coefficient, was defined. The effective distribution coefficient was subsequently compared to the distribution coefficient corresponding to equilibrium conditions, thus showing the deviation of the experimental condition from equilibrium.

Freezing rates in the range from 7×10^{-4} cm/sec to 2×10^{-4} cm/sec were utilized. For agitated solutions, the solute separation attained at a freezing rate of 2×10^{-4} cm/sec was close to the ideal separation obtainable under equilibrium conditions.

Micro-organisms also distribute themselves in agitated urine in such a manner that the last portion to freeze contains the largest number of micro-organisms per unit volume. Freezing, however, is not believed to provide an adequate separation of bacteria. Other methods of sterilization such as filtering and/or ultraviolet irradiation should prove more effective.

Though the attainable solute separation of urine varied with initial solute concentration, it was possible to derive an average value for the distribution coefficient from which the efficiency of a number of freezing schemes could be calculated. It was found that for yields of 50 to 80 per cent of the original urine volume, the equivalent of 12 to 15 liters of liquid had to be frozen in order to recover 1 liter of potable water. It was found that this figure corresponds closely to the energy requirement for a system involving a two-cycle distillation recovery process. Based upon the assumption that the problems of phase separation in a reiterative freezing recovery system are less involved and require a smaller amount of effort than is required for phase separation in a system using distillation, recommendations were made for further study of design parameters of a water recovery system using reiterative freezing or a combination of reiterative freezing and another method of water recovery.

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APPENDIX I

CALCULATION OF THE SOLUTE DISTRIBUTION FUNCTION FROM EXPERIMENTAL DATA

In the experiments performed in this project, no means of monitoring or measuring the continuous change of concentration along the freezing interface is provided. Knowledge of this continuous change is obtained only through measurement of the average concentration of a finite number of fractions which are assumed to contain a linear gradient of concentration, with the average concentration existing at the center of each fraction.

The equation for continuous solute concentration distribution,

$$C_s = kC_o(1-g)^{k-1}$$

then becomes

$$\log \overline{P}_i = \log k + (k-1) \log \overline{w}_i$$

where

$\overline{P}_i$ = normalized concentration at the center of section i

$\overline{w}_i$ = the fraction of charge, measured to the center of section i

$\overline{P}_i$ and $\overline{w}_i$ are defined as follows:

$$\overline{P}_i = \frac{\overline{C}_i}{C_o}$$

where $\overline{C}_i$ = the average concentration of section i

$$\overline{w}_i = 1 - \overline{g}_i$$

where g_i = the fraction which has frozen, measuring from the initially-freezing (dilute) end of the charge to the center of section i, and is given by the equation

$$\overline{g}_i = \frac{\overline{m}_i}{M_o}$$

where

$\overline{m}_i$ = the weight of the frozen charge from the dilute end to the center of section i

M_o = the weight of the whole charge before sectioning

The weight m_i is given by

$$m_i = \frac{1}{2} M_i + (i - 1) \frac{\Delta M_o}{n-1} + \sum_{j=1}^{i-1} M_j$$

where

M_i = the weight of section i

n = the total number of sections

ΔM_o = the weight loss due to slicing

M_j = the weight of section j

The subscripts i and j refer to a numerical sequence of sections, from section 1 at the dilute end to section n at the concentrated end of the charge.

The assumption that the average concentration of each slice equals the "continuous" concentration at the center of that slice is tested in the following manner:

The average concentration of a slice from w_{i-1} to w_i is

$$\overline{P}_i = \frac{k \int_{w_i}^{w_{i-1}} w^{k-1} \, dw}{\int_{w_i}^{w_{i-1}} dw} = \frac{w_{i-1}{}^k - w_i{}^k}{w_{i-1} - w_i}$$

The concentration at the center of slice i is

$$P_i = k\,\overline{w}_i^{\,k-1}$$

The above equations are based on a distribution coefficient "k" which does not vary with concentration. Figure 18 is a plot of the above two equations for several values of k. The calculations are based upon w_i values resulting from five equal sections, with a ten per cent loss due to sectioning apportioned equally to each slice. These considerations yield w_i value pairs of 0 and 0.18, 0.205 and 0.385, 0.410 and 0.590, 0.615 and 0.795, and 0.820 and 1.000.

The graph shows that the approximation causes no appreciable error for values of w larger then 0.15, and that the most accurate method of determining the distribution coefficient is by the intercept with the $\log_{10} w = 0$ line.

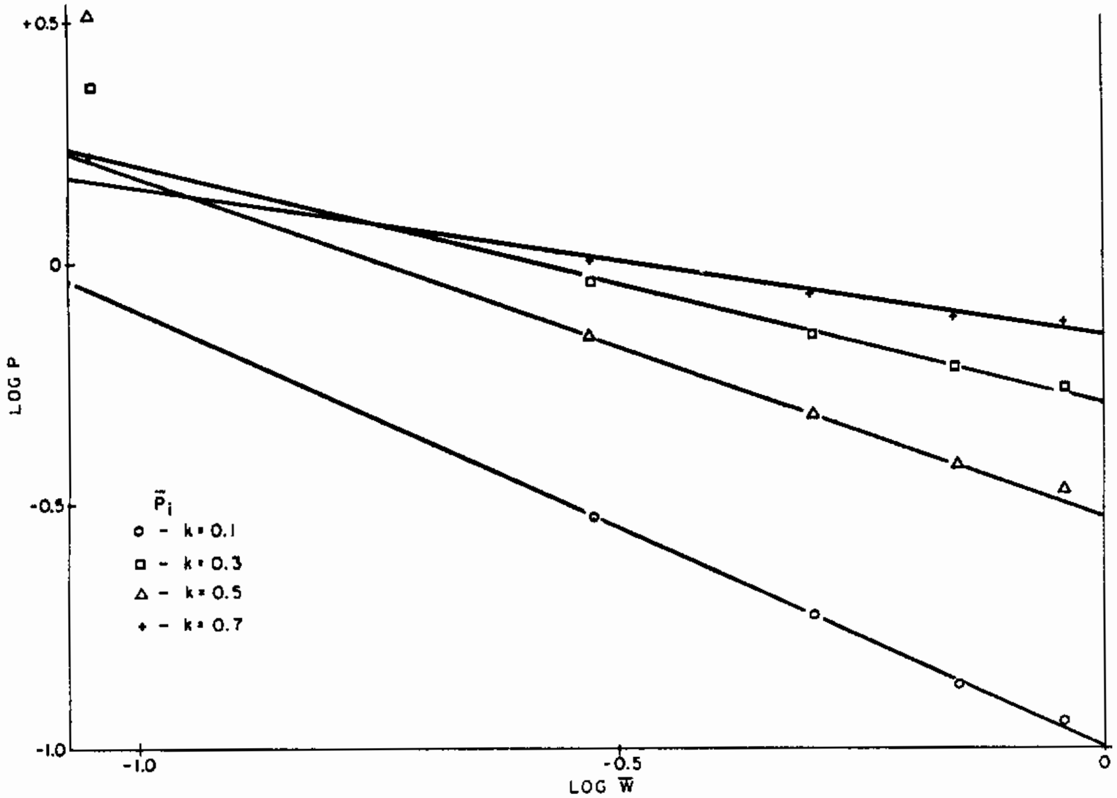

Figure 18. A Plot of the $\overline{P}_i$ Points on the P_i Lines for Several Values of k

APPENDIX II

SOLUTE DISTRIBUTION IN MULTI-PASS ZONE REFINING

(Reprinted with permission from W. G. Pfann, Reiterative Freezing, John Wiley and Sons, New York, 1958.)

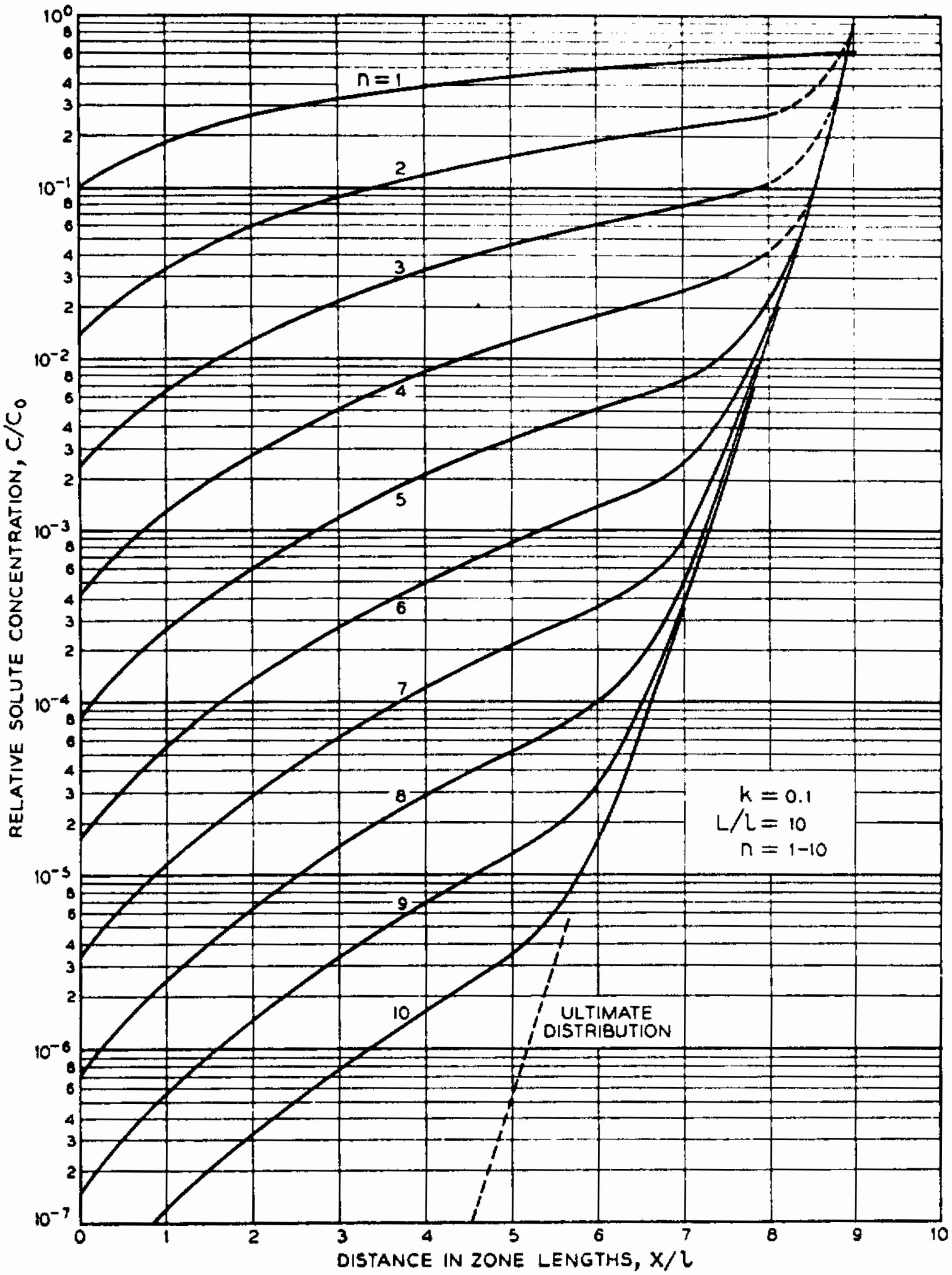

Figure 19. Relative Solute Concentration (C/C_0)(logarithmic scale) Versus Distance in Zone Lengths (x/ℓ) from Beginning of Charge for Various Numbers of Passes (n) (L denotes charge length)

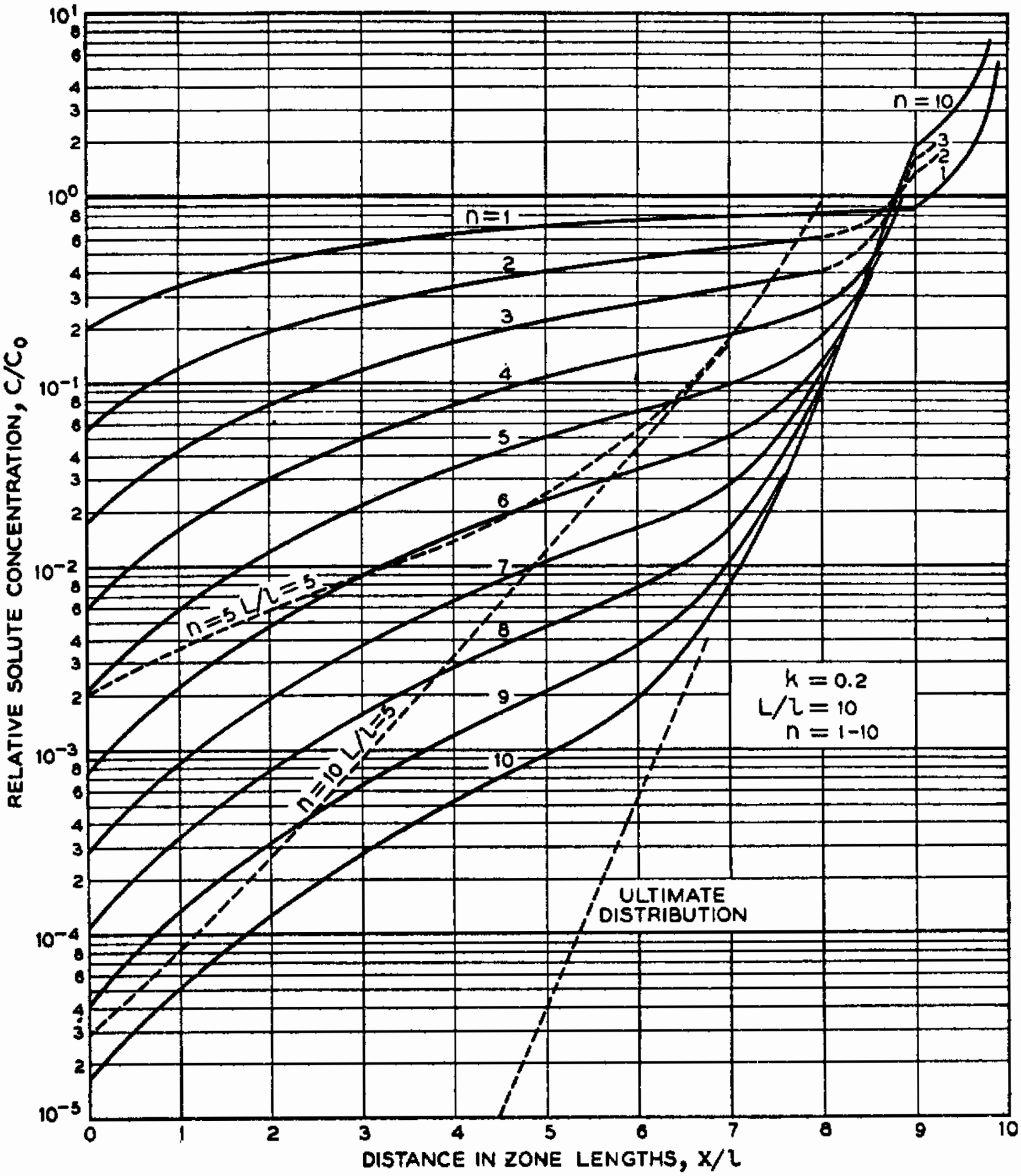

Figure 20. Relative Solute Concentration (C/C_0)(logarithmic scale) Versus Distance in Zone Lengths (x/ℓ) from Beginning of Charge for Various Numbers of Passes (n) (L denotes charge length)

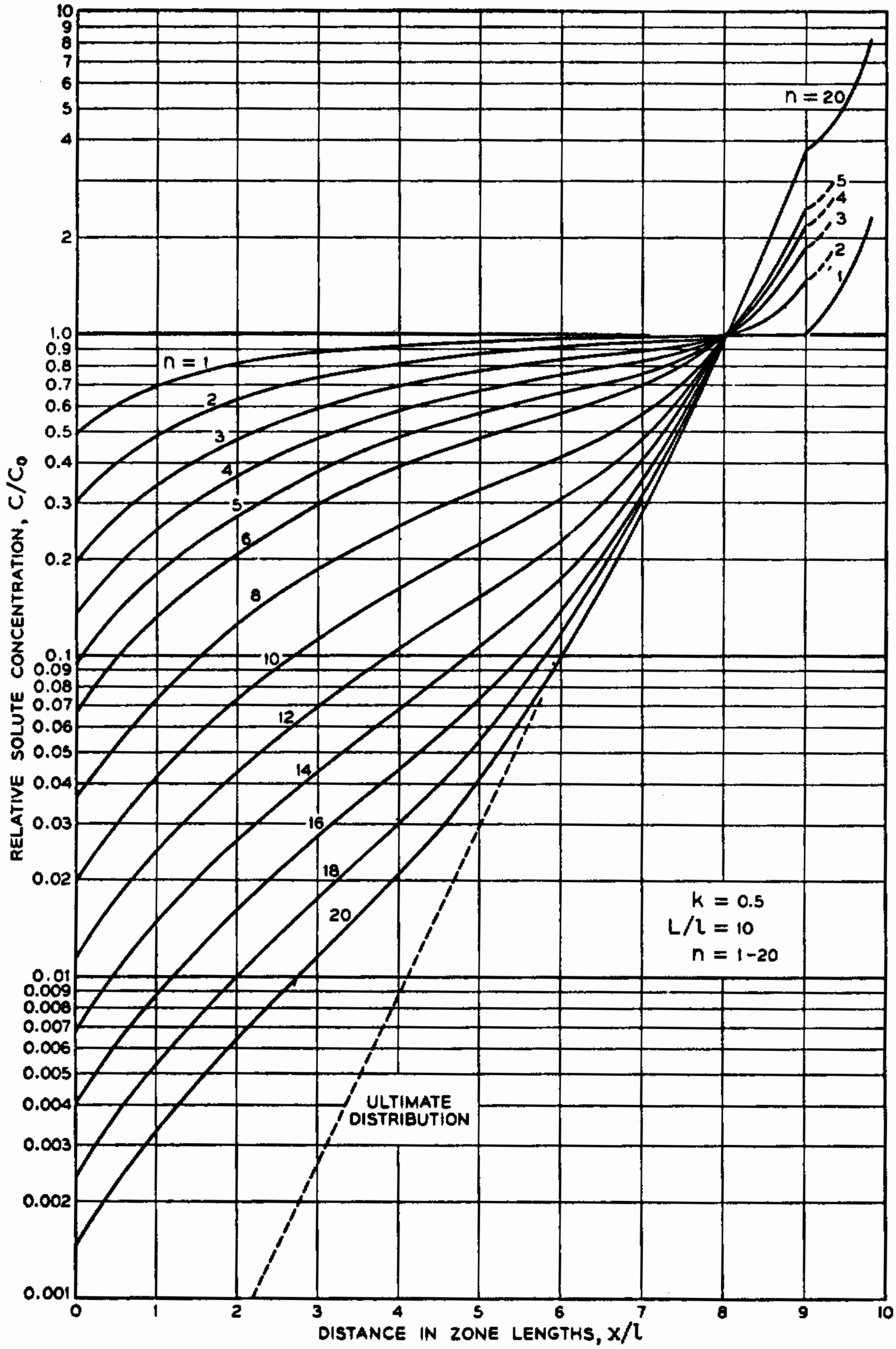

Figure 21. Relative Solute Concentration (C/C_0)(logarithmic scale) Versus Distance in Zone Lengths (x/ℓ) from Beginning of Charge for Various Numbers of Passes (n) (L denotes charge length)

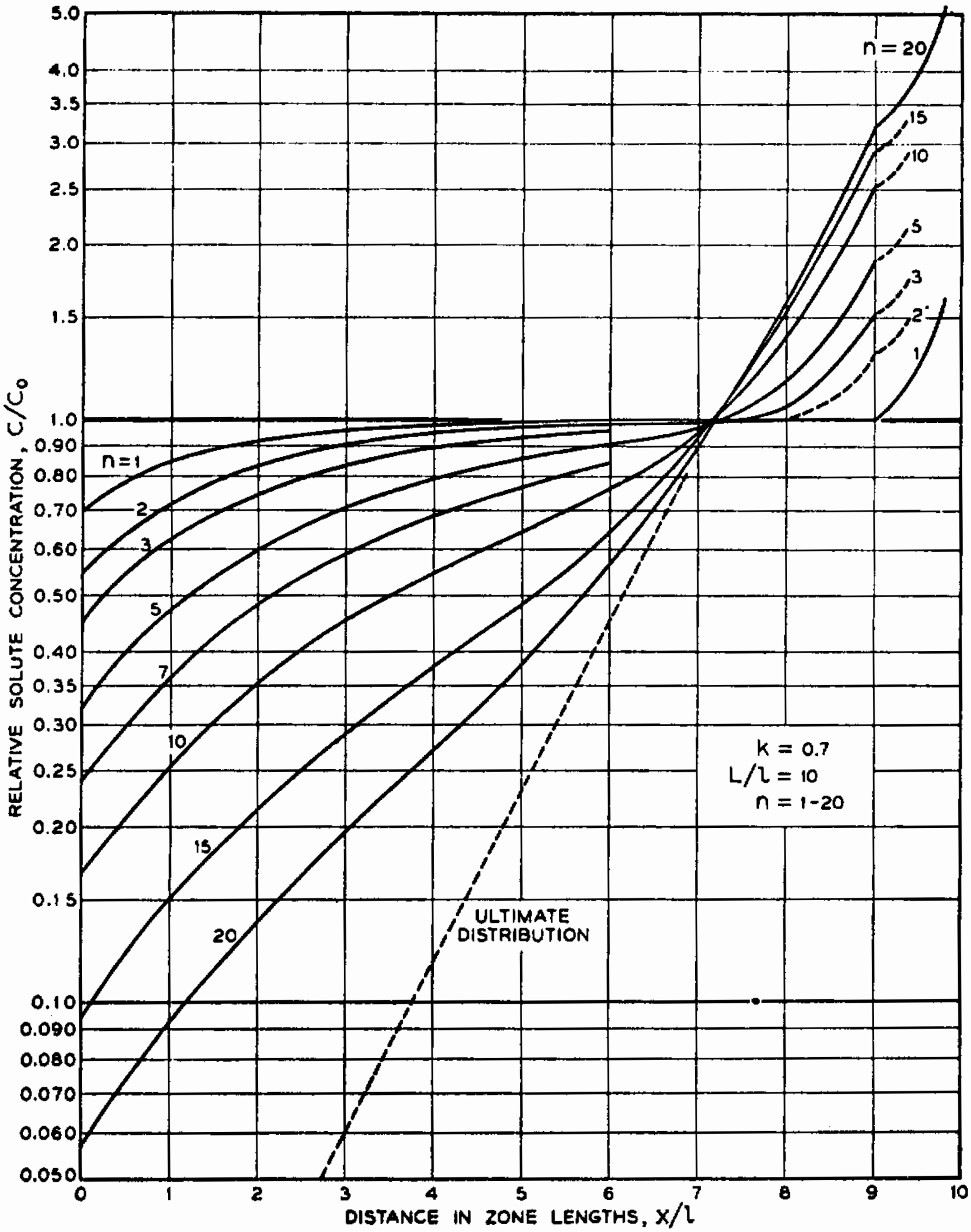

Figure 22. Relative Solute Concentration (C/C_0)(logarithmic scale) Versus Distance in Zone Lengths (x/ℓ) from Beginning of Charge for Various Numbers of Passes (n)(L denotes charge length)

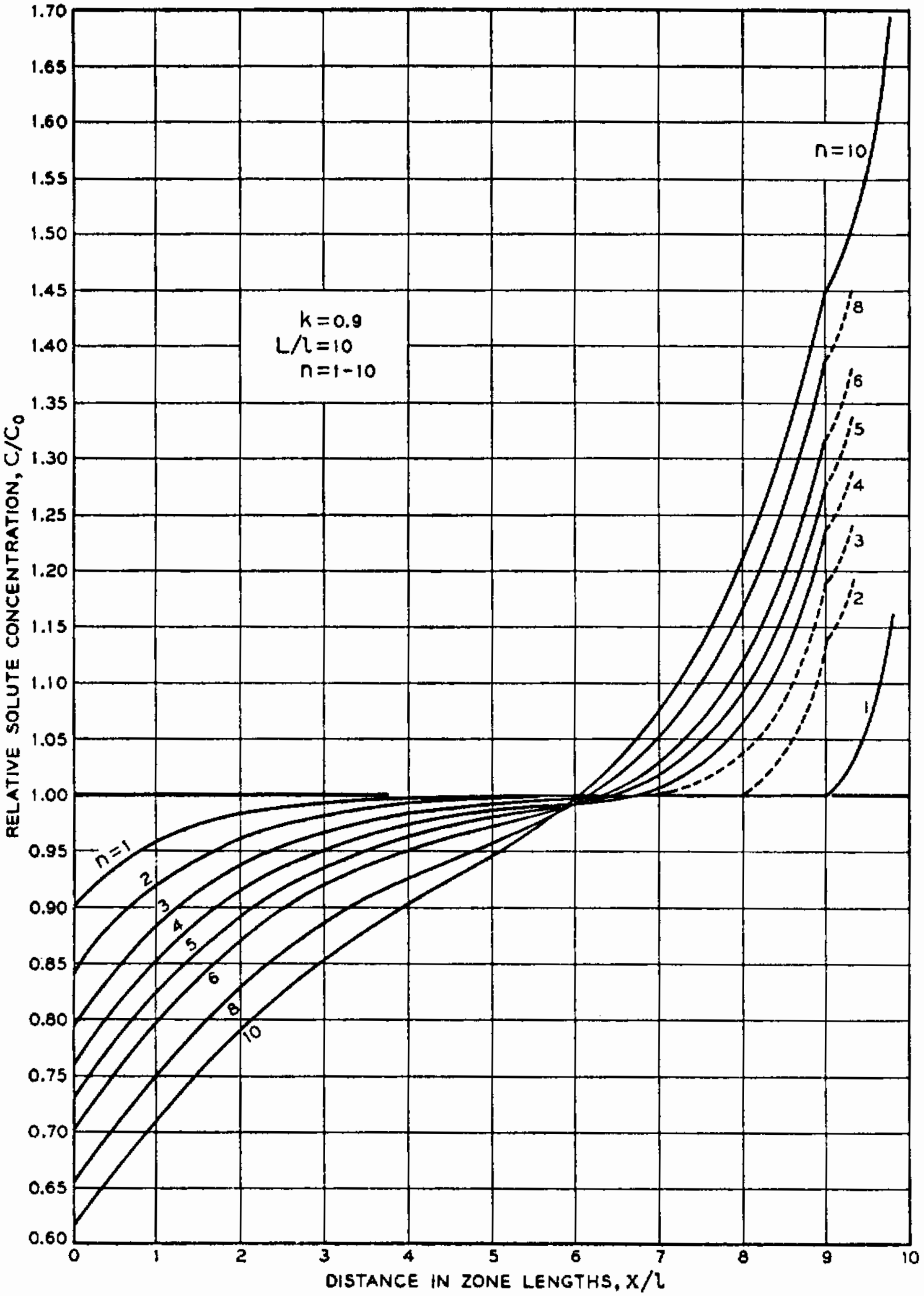

Figure 23. Relative Solute Concentration (C/C_0)(arithmetic scale) Versus Distance in Zone Lengths (x/ℓ) from Beginning of Charge for Various Numbers of Passes (n)(L denotes charge length)

APPENDIX III
REPRESENTATIVE EXPERIMENTAL RESULTS

APPENDIX III
REPRESENTATIVE EXPERIMENTAL RESULTS

The values of the effective distribution coefficient corresponding to each set of experimental data may be derived from the linear plots of $\log_{10} \overline{w}_i$ versus $\log_{10} \overline{P}_i$. $\overline{P}_i$ is the average concentration of slice i expressed as a fraction of the initital solute concentration; $\overline{w}_i$ is the fraction of the total charge which remains to be frozen, from the end of the charge to the center of slice i. (See Appendix I for the mathematical definition of these parameters.)

Table 7. Representative Experimental Results

Run No.	Remarks	Solute	Freezing Rate (cm/sec)	Initial Concentration (gms/100 ml)	$\overline{P}_i$, Fraction of Initial Concentration	$\overline{w}_i$, Fraction Remaining to Freeze
15	No agitation	Sodium chloride	7×10^{-4}	1.0	0.968 1.00 1.01	0.917 0.624 0.207
20	No agitation	Sodium chloride	5×10^{-5}	1.0	0.65 1.04 1.32	0.893 0.479 0.086
17	No agitation	Sodium chloride	7×10^{-4}	1.6	0.99 0.95 0.99 1.07	0.867 0.596 0.370 0.128
19	No agitation	Sodium chloride	5×10^{-5}	1.6	0.83 0.88 1.12 1.27	0.912 0.612 0.305 0.061
29	No agitation	Sodium chloride	7×10^{-4}	4.0	0.790 0.823 0.965 1.47	0.883 0.616 0.356 0.110
18	No agitation	Sodium chloride	5×10^{-5}	4.0	0.833 0.917 1.19	0.853 0.534 0.160
27	No agitation	Urea	5×10^{-4}	1.0	0.73 0.96 1.00 1.40	0.867 0.586 0.349 0.117
25	No agitation	Urea	5×10^{-4}	2.0	0.755 0.850 0.895 1.46	0.900 0.660 0.400 0.122
26	No agitation	Urea	5×10^{-5}	2.0	0.650 0.820 0.811 1.83	0.869 0.592 0.342 0.104
24	No agitation	Urea	5×10^{-4}	5.0	0.88 1.01 1.05 1.05	0.891 0.640 0.387 0.124
23	No agitation	Urea	5×10^{-5}	5.0	0.765 0.871 0.903 1.47	0.894 0.650 0.382 0.113

Table 7. (cont)

Run No.	Remarks	Solute	Freezing Rate	Initial Concen-tration	$\overline{P}_i$	$\overline{w}_i$
22	No agitation	Urea	5×10^{-4}	10.0	0.96 1.01 1.03 1.00	0.895 0.670 0.424 0.133
21	No agitation	Urea	5×10^{-5}	10.0	0.892 0.934 1.06 1.15	0.885 0.643 0.383 0.116
47	Agitation	Sodium chloride	5×10^{-4}	1.6	0.580 0.747 0.805 0.925 2.24	0.931 0.711 0.476 0.257 0.062
55	Agitation and reverse direction	Sodium chloride	2×10^{-4}	1.6	0.400 0.539 0.823 1.48 2.47	0.929 0.748 0.467 0.192 0.044
44	Agitation	Sodium chloride	2×10^{-4}	1.0	0.286 0.375 0.570 1.32 2.84	0.933 0.728 0.489 0.260 0.066
43	Agitation	Sodium chloride	2×10^{-4}	2.0	0.420 0.576 0.750 1.00 2.82	0.921 0.680 0.431 0.232 0.060
35	Agitation	Sodium chloride	5×10^{-4}	4.0	0.596 0.676 0.695 0.841 1.81	0.938 0.763 0.591 0.366 0.099
42	Agitation	Sodium chloride	3×10^{-4}	4.0	0.596 0.671 0.865 1.94	0.893 0.617 0.337 0.092
52	Agitation	Sodium chloride	1.5×10^{-4}	4.0	0.586 0.620 0.749 1.05 2.02	0.922 0.721 0.509 0.292 0.081

Table 7. (cont)

Run No.	Remarks	Solute	Freezing Rate	Initial Concentration	$\bar{P}_i$	$\bar{w}_i$
45	Agitation	Sodium chloride	2×10^{-4}	8.0	0.649 0.705 0.767 1.14 1.86	0.954 0.792 0.558 0.280 0.059
34	Agitation	Urea	5×10^{-4}	1.0	0.49 0.60 0.68 0.90 2.07	0.929 0.752 0.561 0.338 0.100
41	Agitation	Urea	2×10^{-4}	1.0	0.35 0.38 0.60 0.95 2.46	0.928 0.733 0.514 0.306 0.097
33	Agitation	Urea	5×10^{-4}	2.0	0.530 0.662 0.783 1.05 2.04	0.894 0.651 0.467 0.296 0.086
38	Agitation	Urea	2×10^{-4}	2.0	0.449 0.495 0.696 0.843 1.86	0.944 0.789 0.609 0.372 0.108
59	Agitation and reverse direction	Urea	2×10^{-4}	2.0	0.407 0.407 1.15 1.43 2.24	0.879 0.635 0.466 0.246 0.035
32	Agitation	Urea	5×10^{-4}	5.0	0.759 0.653 0.678 0.951 2.00	0.923 0.732 0.520 0.296 0.084
51	Agitation	Urea	2×10^{-4}	5.0	0.539 0.561 0.678 0.950 1.81	0.935 0.737 0.529 0.348 0.123

Table 7. (cont)

Run No.	Remarks	Solute	Freezing Rate	Initial Concentration	$\bar{P}_i$	$\bar{w}_i$
68	Agitation	Urine equivalent solution	2×10^{-4}	4.0	0.582 0.580 0.668 0.840 2.51	0.922 0.709 0.463 0.258 0.091
69	Agitation and reverse direction	Urine equivalent solution	2×10^{-4}	4.0	0.575 0.578 0.528 0.782 1.84	0.921 0.712 0.515 0.324 0.101
76	Agitation	Urine	7×10^{-4}	4.9	0.699 0.732 0.714 1.15 2.37	0.932 0.772 0.492 0.212 0.059
78	Agitation	Urine	2×10^{-4}	4.9	0.624 0.622 0.681 0.985 2.07	0.921 0.719 0.484 0.275 0.089
74	Agitation	Urine diluted with water 1:1	7×10^{-4}	2.4	0.630 0.721 0.756 0.860 2.50	0.922 0.736 0.548 0.294 0.060
83	Agitation	Urine diluted with water 1:1	2×10^{-4}	2.4	0.515 0.568 0.677 1.16 3.40	0.887 0.642 0.414 0.208 0.048
77	Agitation	Urine diluted with water 1:3	7×10^{-4}	1.2	0.459 0.523 0.465 0.494 3.40	0.942 0.781 0.601 0.339 0.076
80	Agitation	Urine diluted with water 1:3	2×10^{-4}	1.2	0.392 0.400 0.650 2.86	0.933 0.673 0.342 0.095

Table 7. (cont)

Run No.	Remarks	Solute	Freezing Rate	Initial Concentration	$\overline{P}_i$	$\overline{w}_i$
79	Agitation	Urine diluted with water 1:9	7×10^{-4}	0.49	0.796 0.694 0.653 0.898 2.26	0.899 0.690 0.471 0.257 0.077
82	Agitation	Urine diluted with water 1:9	2×10^{-4}	0.49	0.128 0.154 0.231 1.10 3.08	0.918 0.736 0.553 0.323 0.089