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CLUSIUS-DICKEL SEPARATIONS (CDS): A NEW LOOK AT AN OLD TECHNIQUE

FINAL REPORT

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FOREWORD

This document is the final report for Contract NAS8-29609 and was prepared for the National Aeronautics and Space Administration, Marshall Space Flight Center, by personnel of Lockheed Missiles & Space Company, Inc., Huntsville Research & Engineering Center, Huntsville, Alabama.

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NOMENCLATURE

Symbol	Definition	
a	gravity acceleration at a designated point	
A	parameter in equation $q_e = e^{2AL}$ and further defined by $A = H/2K$, cm^{-1}. Also used as a parameter equal to $\alpha \Delta T / 2 \overline{T}$.	
b	gravity gradient, sec^{-2}	
B	CD cell width, cm	
c	mole fraction	
Ci	curies	
d	space between hot and cold walls, cm	
D_{12}	coefficient of ordinary diffusion, cm^2/sec (see note 1)	
D'	liquid thermal diffusion coefficient, cm^2/sec-$^\circ$C (see note 1)	
D_T	gaseous thermal diffusion coefficient, cm^2/sec (see note 1)	
D_c	mole fraction diffusion coefficient	See Appendix G
D_w	weight fraction diffusion coefficient	
D_m	molar concentration diffusion coefficient	
$\mathcal{E}_e$	experimental efficiency	
$\mathcal{E}_o$	limiting energy conversion efficiency	
g	gravity acceleration, cm/sec^2	
g_g	gravity acceleration on earth surface, 980 cm/sec^2	
h	height, cm	
H	transport coefficient in equation $q_e = e^{HL/K}$, gm/sec	
J	mass flux, gm/cm^2-sec	
k	thermal diffusivity, cm^2/sec	
k_T	thermal diffusion ratio, dimensionless	

NOMENCLATURE (Continued)

Symbol	
K	transport coefficient in equation $q_e = e^{HL/K}$. Also $K = K_c + K_d$, gm-cm/sec
K_c	remixing transport coefficient, gm-cm/sec
K_d	cell back diffusion transport coefficient, gm-cm/sec
$\mathcal{L}$	total length of cascade cell, cm
L	length of a single cell, cm
m	molar concentration, moles/liter
MEV	million electron volts
M.Wt.	molecular weight, gm
$\overline{M}$	average molecular weight, gm
P	pressure
Pr	Prandtl number = ν/k, dimensionless
n	number of moles
q	separation factor at time t $\left(= \dfrac{c_e(1-c_s)}{c_s(1-c_e)}\right)$
q_e	separation factor at steady state
Nu	Nusselt number, heat transported/heat transported if conduction were the only means of heat transfer
r_1	radius of outer cylindrical column
r_2	radius of inner cylindrical column
Ra	Rayleigh number = $\dfrac{g\beta\Delta T d^3}{\nu k}$, dimensionless
Re	Reynolds number = $\dfrac{\rho v L}{\mu}$
R	molar gas constant, 1.9872 cal/mole-°K
S_o	limiting entropy efficiency
SW	separative work
v	velocity, cm/sec
t	time

NOMENCLATURE (Continued)

Symbol	
t'_r	time to reach $1/e^{th}$ of the steady state separation factor q_e
T	temperature, ^oK
T'	a temperature different from T
T_H	temperature of the hot wall
T_C	temperature of the cold wall
ΔT	$T_H - T_C$, ^oC or ^oK
$\bar{T}$	mean temperature, $\frac{T_H + T_C}{2}$
USW	unit separative work
w	weight fraction and also 1/2 d
W	one-half amount of feedstock or watts
Greek	
α	thermal diffusion factor
β	coefficient of thermal expansion, $\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$, $(^oC \text{ or } ^oK)^{-1}$
Δ	difference $c_e - c_s$
η	stage number
λ	thermal conductivity, cal/cm^2 sec ^oC/cm
μ	coefficient of viscosity, poise or gm/cm-sec
ρ	density, gm/cm^3
σ	flow rate, gm/sec; or Soret coefficient, $(^oC)^{-1}$
τ	rate of transport of a species, gm/sec
ν	kinematic viscosity, cm^2/sec
χ	mass of gas per unit length of cell, gm/cm
Ω	rotation rate
Subscripts	
opt	optimum
1, 2	species designation or stage number

NOMENCLATURE (Continued)

Subscripts

f	final or feedstock
i	initial or i species
n	initial
c	mole fraction
w	weight fraction
m	molar concentration

Superscripts

o	original or initial

Note: It is easy to become confused reading the literature because definitions of the thermal diffusion factor and coefficient are not always clear. Powers and others, for example, use $\alpha D_{12}/T$ for D'. (The present study also follows Power's convention.) Some have adopted the convention that D' is negative when the heavier component concentrates in the colder regions. The situation regarding concentration units is even more confused. Appendix G indicates the source of the difficulty.

Section 1
INTRODUCTION AND SUMMARY

The Clusius-Dickel (CD)* technique couples thermal diffusion to a countercurrent natural convective flow to effect separation in liquid and gaseous solutions. Materials separable by the technique include:

- Aqueous biological solutions
- Isotopes in both gas and liquid states
- Aqueous solutions of both ionized and un-ionized materials
- Organic solutions
- Liquid metallic solutions
- Fused salt solutions
- Ortho and para-hydrogen mixtures

The technique was discovered in the late 1930s by K. Clusius and G. Dickel but fell into relative obscurity for commercial applications about 20 years after its discovery. The reasons for its decline included a number of deleterious apparatus and operating features, among which were large power requirements, costly equipment construction, and small processing volumes. The present study, however, after critically reexamining the CDS* technique, concludes that the objectionable features of the technique can probably be circumvented by a number of means among which are: (1) conducting the CD operation in space environments; (2) utilizing modified cell designs; and (3) combining the CD technique with other separative techniques or principles, i.e., electrophoresis, field flow fractionation (FFF), adsorption (parametric pumping), and chemical reactions. Means (2) and (3) would benefit still further from space environments. It is also concluded that the potential of the technique for separations of biological and other aqueous solutions has been largely overlooked. The CD principle appears further to offer novel earth applications such as solar water desalination, energy conversion devices, and a use for waste heat.

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*CD = Clusius-Dickel; CDS = Clusius-Dickel Separation.

This document reviews the history, applications, and theoretical basis of the technique. The advantages to be realized by conduction of CDSs in low-g, space environments are then deduced. The low-g space advantages so identified are:

- Reduced convective flow velocities in low-g environments will allow larger cell wall spacings allowing in turn larger processing volumes (throughputs) and avoidance of deleterious "parasitic" remixing.
- Power requirements will be supplied "free" by solar heating and radiation cooling.
- Larger allowable cell wall spacings will reduce equipment construction costs.
- Lack of gravity-induced mechanical stresses will allow longer cell lengths to be utilized thereby increasing size of processing volumes.
- A possibility of conducting CDS with free floating liquid spheres.

This document also reports the results of investigations aimed at further improving CDS efficiencies by altering convective flow patterns. The question of whether multicellular flow or turbulence can introduce a new separation mechanism which would boost separation efficiencies at least an order of magnitude is considered briefly. The results indicate that certain multicellular flow patterns probably can increase separation efficiencies. Experimental verification of multicellular efficacy, however, has not yet been accomplished primarily because of difficulties in defining required boundary conditions for a given multicellular flow pattern.

The findings of the present study also indicate the CDS technique holds the promise of finding unusual application in the areas of biological and polymer separations. Biological and polymer solutes generally have high thermal diffusion factors and thus can be readily separated with low power consumption. Furthermore, the ability of the technique to separate solute molecules on the basis of shape differences alone should present very interesting possibilities for separations of complicated biological materials such as DNA molecules, viruses, and "B" and "T" lymphocytes. The possibility of combining CDS with other techniques, especially the FFF technique, offers further exciting possibilities.

The Soret effect or thermal diffusion can generate potential gradients in electrolytic solutions. Non-convective liquid thermocells, therefore, can convert heat into electricity. It has been reported by others that such a cell utilizing lead electrodes and sulfuric acid can attain an efficiency of 6.16%, comparable to 10% for the best thermoelectric generators currently used. The present study speculates that introducing electrodes into a CD column that is separating electrolyte holds the possibility of a self-renewing concentration cell run by solar power.

Finally, the CD principle appears to offer earth applications in the areas of water desalination and a use for waste heat.

It is also interesting to note that the Russians also appear to be rediscovering the CD technique as evidenced by some ten recent papers. (See Bibliography).

Section 2
HISTORY OF CDS

In 1856 C. Ludwig discovered that a temperature gradient can separate components of a liquid solution. Ludwig heated one leg of an inverted U-tube filled with an aqueous solution of sodium sulfate and cooled the other. After a few days crystals of sodium sulfate were seen to form in the cooled leg. In 1879, C. Soret, apparently unaware of Ludwig's work, studied the phenomenon more extensively. The separation of components in liquid solution by a thermal gradient subsequently became known as the Soret effect. Although J.H. van't Hoff offered one explanation of the effect in 1887, a satisfactory theory for the effect in liquids is still lacking. A temperature gradient separative effect in gases was predicted theoretically by D. Enskog and S. Chapman almost simultaneously in 1911-12 and was subsequently confirmed experimentally in 1917. The phenomenon in gases is usually called thermal diffusion. It may be mentioned, however, that a variety of terms is currently in use to indicate separation by means of a thermal gradient. These include Soret effect, Soret diffusion, thermal diffusion, thermodiffusion, thermotransport, thermal transport and thermophoresis. The present work will generally use the term thermal diffusion regardless of whether the separation takes place in the liquid or gas phase.

Thermal diffusion by itself is a very slow and inefficient process (see Appendix A for theoretical details). The inefficiency of the process is readily understandable when we consider that the separating force generated by a thermal gradient is opposed by a remixing force generated by ordinary diffusion. The separations achievable by thermal diffusion alone are of the order of several percent or frequently only a few parts per thousand (Ref. 1, p. 273). Separations in static cells, i.e., cells in which no fluid flow occurs, therefore, never have become a practical technique. In 1938, however, K. Clusius and G. Dickel discovered that if a countercurrent, natural convective flow is coupled with thermal diffusion, separation speed and efficiency can be increased by orders of magnitude. Using a convective column that was 36 meters long Clusius and Dickel increased the separation of $HC\ell^{35}$ from $HC\ell^{37}$ by a factor of 4000 over that obtainable in a non-convective cell. Separation of a large variety of materials was investigated soon after announcement of the discovery. The types of cells used were either flat plate cells or cylindrical cells, in which the solution to be separated was contained in the annulus between two co-axial cylinders. The essential elements of an apparatus which illustrates the principles involved is shown in the following schematic.

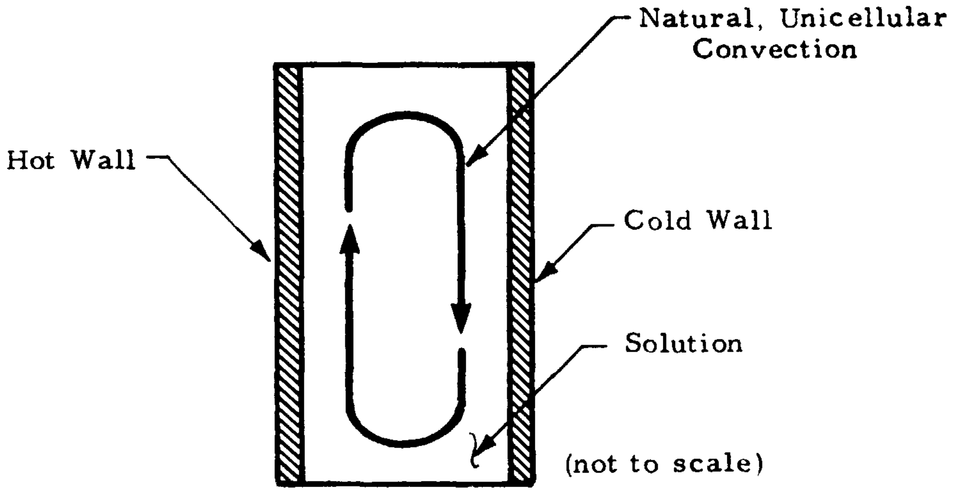

Fig. 1 - Schematic of CD Cell Essentials

To understand how a countercurrent convective flow enhances separation, consider first the situation where no flow is present. In such a case, one component of the solution migrates toward the hot wall while the other migrates toward the cold wall. The migration, however, eventually halts as back diffusion gradually builds up. A final steady state concentration gradient eventually results, i.e., eventually the rate at which molecules migrate because of thermal diffusion becomes equal to the rate of a counter mass diffusion. If now a countercurrent flow is introduced, molecules migrating toward the cold or hot walls are removed faster near the wall than they are near the center of the cell by downward or upward flowing currents. Back mass diffusion is thereby reduced. If convection is too fast, a remixing effect due to flow can predominate. Obviously, an optimum flow rate or convective velocity exists (mathematical details are given in Appendix B).

The discovery of the enhanced separation effect of convection by Clusius and Dickel just before World War II led to the method being intensively explored in the next decade as a means of separation of uranium isotopes. Because of the wartime security the work was highly secret and publications did not appear until after the war. In publications appearing after the war it is reported that a plant had been constructed as part of the Manhattan project which enriched normal uranium containing 0.715% U^{235} to 0.86%. The plant consisted of 2100 separation columns, each about 48 feet long. The uranium was processed as uranium hexafluoride. The plant was in operation for about six months, and then was dismantled when CDS was displaced by the gaseous diffusion enrichment method. The principal drawbacks of conventional CDS for uranium enrichment are the long relaxation times (time required to attain near equilibrium) and the high heat consumption. The power cost alone for CDS was found to be about 100 times greater than the total cost of separative work by gaseous diffusion (Ref. 2).

During the 50s the technique was explored for various separations and fractionations of petroleum and associated products (see Appendix D for specific separations). Because of the high power requirement, however, this area of application also faded. As far as is known, CDS is utilized commercially presently only for the separation of rare gaseous isotopes and for purification of inertial guidance fluid.

Although CDS is currently a relatively obscure technique, the Soret effect is experiencing a resurgence of interest. A number of papers have appeared recently dealing with the role of the Soret effect in phenomena such as double diffusive convection and crystallization.

It may be mentioned incidently that CDS is also referred to as "thermogravitational separation" in the literature. More extensive historical discussions of both the CDS technique and the Soret effect will be found in the general references given in the Bibliography.

Section 3

SEPARATIONS POSSIBLE BY THE CD TECHNIQUE

The CD technique lends itself to separations in both the liquid and gaseous phases. The intriguing aspect of CDS is that separation depends not only on the relative masses of the constituents to be separated but also on their atomic composition and molecular shapes. Thus not only molecules of differing masses but also molecules of identical masses but differing in atomic species or in arrangement of atoms, i.e., isomers, can be separated using this method. Also, with ternary or higher multicomponent mixtures, varying degrees of fractionation can be achieved.

The theory of thermal diffusion is fairly well established for gases, and calculation of thermal diffusion factors by means of various formulas is possible. For liquids, on the other hand, no general theory exists and it is necessary to either consult the literature to see if a certain separation is feasible or to determine the feasibility experimentally.

The range of separations possible by CDS is indicated by the following list.

Liquid Phase Separations

Biological solutions and suspensions (viruses, carbohydrates, esters, polysaccharides, enzymes, etc.)

Aqueous electrolytic solutions (water solutions of NaCℓ, $CuSO_4$, etc.)

Aqueous non-electrolytic solutions (alcohol and water)

Polymer solutions (polystyrene in toluene)

Organic isomers (ortho, meta, and para xylene, cis-trans isomers, etc.)

Binary and ternary organic mixtures (cetane and cumene, benzene and n-heptane, etc.)

Oil fractionations (talloil, white oil, paraffinic oils, etc.)

Isotopic solutions (D_2O from H_2O, $C^{32}S_2$ from $C^{34}S^{32}S$, $^{235}UF_6$ from $^{238}UF_6$, etc.)

Molten salt solutions

Liquid metal solutions

Gas Phase Separation

Isotopic mixtures (D_2 from H_2, ^3He from ^4He, $^{16,18}O_2$ from $^{16}O_2$, etc.)

Various gas mixtures (Br_2 and Cl_2 from noble gases, argon from neon, etc.)

Ortho and para hydrogen

In Appendix D a comprehensive bibliography of a large number of specific separations that have been reported in the literature is given.

Section 4
OPERATIONAL PARAMETERS OF CONVENTIONAL CD CELLS

General Relationships

The theory developed in the early 40s by Furry, Jones, and Onsager (FJO) (Ref. 3) for CD cells can serve to give a general, qualitative "feel" for what degrees of separation, in what time intervals, are possible. It should be emphasized, however, that the FJO theory is only as valid as the validity of its assumptions. Probably the most important experimental control that must be maintained, if the FJO theory is to apply, is that of the convective flow pattern. The FJO theory assumes a laminar, unicell type of convection. Deviations from this type flow pattern can have either pronounced deleterious (parasitic) or possibly desirable effects depending on the particular deviation. On earth CD operation is notoriously sensitive to parasitic effects. Enhancement of separation efficiencies by flow patterns other than laminar unicellular, on the other hand, occurs spuriously and has not as yet been conclusively demonstrated experimentally. The question of flow pattern on separation has been considered only cursorily in the literature. Experimental and theoretical work conducted in the course of the present study, as well as some reports in the literature of improved separations as the result of turbulence, however, indicate that flow patterns other than unicellular may result in better separations. Both of these aspects of CDS are considered further in a following section. In the present section the FJO theory will be utilized to indicate generally how conventional CD cells work with different material systems and how parameters such as column length, temperature difference, slit width, and gravity level affect separation levels and times.

The separation parameters that are of present primary interest are the following:

q	transient separation factor
q_e	separation factor at steady state or maximum separation attainable in a given cell
t	time to reach a separation factor of q
t'_r	relaxation time to reach $1/e^{th}$ of the steady state factor q_e

The separation factors q and q_e are defined by the following relationship:

$$q = \frac{c_e(1 - c_s)}{c_s(1 - c_e)}$$

where c_e is the mole or weight fraction of a given component in the enriching part of the cell, and c_s is the corresponding concentration in the stripping part of the cell. If q is rewritten as

$$q = \frac{(c_e/1 - c_e)}{(c_s/1 - c_s)}$$

it is readily seen that q represents a relative separation. The following simple example illustrates further the meaning of q. Suppose a solution containing 4% by weight of solute is separated so that at the enriching end a 6% solution is obtained and a 2% solution is obtained at the stripping end. The q factor for such a separation would be 6.

The lighter component of a bicomponent mixture usually concentrates at the top of a cell and the heavier at the bottom, i.e., the mixture is enriched at the top with lighter component and stripped of the lighter component at the bottom. The separation factor can vary from one, which indicates no separation, to values in the millions or more. However, as will soon be seen, extraordinarily huge values of q are generally accompanied by huge values of relaxation times. Practical values of q, which give reasonable separation times, range from about 1.001 to 3000. The range 2 to 5, however, appears as the most favorable for achieving reasonable separations in reasonable times.

The separation factors and relaxation times depend on a number of factors, including cell geometry and construction. The theoretical dependencies of the separation factors and the relaxation times on the various column, operational, and material parameters are outlined in Appendix B. With the aid of the theoretical relationships presented in Appendix B it is possible to define optimum values of various operating parameters. For example, for a given solution and a given temperature difference, the spacing, d, between the hot and cold wall which will result in optimum separation at steady state is given by

$$d_{opt} = \left(\frac{9!}{2}\right)^{1/6} \left(\frac{\mu D_{12}}{\bar{\rho} g \beta \Delta T}\right)^{1/3}$$

Alternatively, to calculate an optimum gravity level for a given annular spacing, the following relationship applies (Appendix B)

$$g_{opt} = \frac{\sqrt{9!}\, \mu D_{12}}{\bar{\rho} \beta d^3 \Delta T}$$

or

$$\frac{\sqrt{2}\, d^3}{d_{opt}^3} = \frac{g}{g_{opt}}$$

In order to maintain the required unicellular flow pattern, the cell should not have parameters which would result in a Reynolds number, Re, more than 25. If the Re exceeds 25, turbulence ensues. Turbulence in a conventional CD cell would mean remixing and decrease separation efficiency. The condition that Re < 25 can be restated (Appendix B) as

$$\frac{g}{g_{opt}} < 12.5$$

Practically, values of g/g_{opt} less than about 5 should be sought to be on the safe side. The present study, however, for calculational convenience sets the value of g/g_{opt} that is not to be exceeded at 10. Interestingly enough, more efficient operation ensues at larger g/g_{opt} values than at smaller values (Ref. 3, p. 173).

In the following subsections example calculations for both single stage and multistage CDS are given. Production CDSs are usually continuous, cascade operations, i.e., a number of separation cells are arranged in some sort of a pyramid fashion and continuously fed at one end and products and stripped solutions taken out at the other end. Although single stage CD cells are usually used for research or laboratory purposes, they may be considered production units if the amount of product required is small.

Example Calculations Illustrating Single Stage Operation

In Table 1 some examples of single stage CDS are presented for instructive and comparison purposes. Single stage operation can be conducted in a variety of cells which may or may not include reservoirs. In the present study only two types of single stage cells are considered. One type is a flat plate cell without reservoirs. (In Appendix B the modification that must be made to the mathematics of a flat plate cell to render them suitable for cylindrical cells without reservoirs is briefly indicated.) The other type cell considered is a flat plate cell with an infinite reservoir attached to the stripping end of the cell. Mathematical formulas for both type cells are given in Appendix B. The important difference between the two types of cells to be considered for present purposes is that the cell with an infinite reservoir at one end is capable of maintaining the concentration at that end at some constant, initial value. In the cells without reservoirs, concentrations vary throughout the cell as separation proceeds until a steady state condition is reached. The cell with an infinite reservoir attached to one end represents a somewhat more realistic case for large production type operations, as will be subsequently evident. The cell without reservoirs is of interest for small scale laboratory type operations.

The material properties used in the calculations of Table 1 are given in Table 2.

Table I

EXAMPLE CALCULATIONS ILLUSTRATING CDS SINGLE STAGE OPERATION UNDER A VARIETY OF CONDITIONS

System	System Type	Case No.	d (cm)	ΔT (^{o}C or ^{o}K)	L (cm)	g ($-g_g$)	g/g_{opt}	q_e	One Infinite Reservoir t_r' (days)	No Reservoir t_r' (days)	q	One Infinite Reservoir (days)
Copper Sulfate in Water	Aqueous Electrolytic	A1	0.721	45	30	9.88×10^{-6}	1	1937	3.2×10^{4}	323		
		A2				9.88×10^{-5}	10	4.57	17	0.92		
		A3				1	1.01×10^{5}		Turbulent			
		A4	1			3.71×10^{-6}	1					
		A5				3.71×10^{-5}	10	2.99	14			
		A6	2			4.63×10^{-7}	1					
		A7				4.63×10^{-6}	10	1.73	12			
		A8	0.0154			1	1					
Sugar in Water	Aqueous Non-Electrolytic	B1	0.0189	65	30	1	1	10^{16}	10^{15}			
		B2	0.4	65	30	3.62×10^{-5}	1					
		B3				3.62×10^{-4}	10	1.76	21			
		B4	0.6			1.07×10^{-5}	1					
		B5				1.07×10^{-4}	10	1.46	20			
Cetane-Cumene	Binary Organic Mixture	C1	0.686	82.2	61	3.42×10^{-6}	1	5055	10^{4}			
		C2				3.42×10^{-5}	10	5.42	19			

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Table 1 (Continued)

System	System Type	Case No.	d (cm)	ΔT (°C or °K)	L (cm)	g ($-g_g$)	g/g_{opt}	q_e	One Infinite Reservoir t_r' (days)	No Reservoir t_r' (days)	q	One Infinite Reservoir (days)
Mercury - 196 Hg from 202 Hg	Metallic Liquid 1 atm pressure	D1	0.0074	100	60	1	1	10^{13}	10^{13}		1.244	seconds
		D2	0.0066 (optimum)			1		10^{14}	10^{14}			
		D3	0.1			1	2.5×10^{3}	Turbulence				
		D4				4×10^{-4}	1	9.72	10^{3}	93		
		D5				4×10^{-3}	10	1.57	24	2	1.244	13
		D6	0.2			5×10^{-5}	1	3.1	10^{3}		1.569	10^{2}
		D7				5×10^{-4}	10	1.25	22			
		D8			120	5×10^{-5}	1					
		D9				5×10^{-4}	10	1.57	96	8		
		D10		200	60	4.5×10^{-5}	1	5.79	10^{2}			
		D11				2.5×10^{-4}	10	1.24	5.6			
Sulfur - 36 S from 32 S	Non-Metallic liquid	E1	0.2013	180	60	1	1	3.44	10^{3}		1.50	317
		E2	1			8×10^{-3}	1	9.42	10^{3}			
		E3				8×10^{-2}	10	1.56	24			

Table 1 (Concluded)

System	System Type	Case No.	d (cm)	ΔT (°C or °F)	L (cm)	g ($\div g_g$)	g/g_{opt}	q_e	One Infinite Reservoir t'_r (days)	No Reservoir t'_r (days)	q	One Infinite Reservoir (days)
Methane - 13 CH_4 from 12 CH_4	Gas 1 atm pressure	F1	0.5271	300	1000	1	1	58.8	39.5			
		F2	1			0.1464	1	8.57	14			
		F3				0.7320	5	2.28	0.63			
Uranium Hexafluoride - 235 UF_6 from 238 UF_6	Liquid pressures up to 200 bars	G1	0.01104	222	1460	1	1	10^8	10^{10}			
		G2	0.025			1×10^{-3}	1	10^{26}	10^{28}		3	seconds
		G3				1	10^3	Turbulence* (4.49)	(167)			
		G4				1×10^{-2}	10	10^5	10^7		3	170
		G5	0.25			1×10^{-5}	1	426	10^6		3	10^3
		G6				1×10^{-4}	10	3.32	10^4			

*See discussion for this particular case

Table 2

MATERIAL PROPERTIES USED IN CALCULATIONS OF TABLE 1

Case	Notes	Density, ρ (gm/cm^3)	Viscosity μ (poise or gm/sec-cm)	Coefficient of Chemical Diffusion D_{12} (cm^2/sec)	Coefficient of Thermal Expansion β (1/°K)	Thermal Diffusion Factor α	Temp. of Hot Wall T_H (°K)	Temp. of Cold Wall T_C (°K)	Mean Temperature, $\overline{T}$ (°K)
Aqueous Copper Sulfate Solution	Concentration 3.172% by weight	1.023	1.09×10^{-2}	5.5×10^{-6}	2.16×10^{-4}	2.9	326	281	303.5
Aqueous Sugar Solution	Concentration 2% by weight of sucrose	1.2	1×10^{-2}	2.94×10^{-6}	1×10^{-4}	0.45	[illegible]3	288	320.5
Cetane-Cumene		0.845	5.44×10^{-3}	2.17×10^{-5}	9.46×10^{-4}	0.97	389	307	348
196 Hg from ^{200}Hg	Natural isotopic abundance 196 0.146% 198 10.02 199 16.84 200 23.13 201 13.22 202 29.80 204 6.85	13.6	1.6×10^{-2}	10^{-5}	1.8×10^{-4}	0.03	381	281	331
^{36}S from ^{32}S	Natural isotopic abundance 32 95.0% 33 0.760 34 4.22 36 0.0136	[illegible]	186	10^{-5}	4.3×10^{-4}	0.03	573	393	483
$^{13}CH_4$ from $^{12}CH_4$	Natural isotopic abundance of carbon 12 98.892% 13 1.108	4.47×10^{-4}	1.51×10^{-4}	0.474	2.24×10^{-3}	0.0077	600	300	450
$^{235}UF_6$ from $^{238}UF_6$	Natural isotopic abundance of uranium 234 0.0058% 235 0.71 238 99.[illegible]%	2	7×10^{-3}	2×10^{-5}	1×10^{-3}	0.005	337	559	448

One feature of the calculations presented in Table 1 which should be immediately apparent is that very large separation factors are impractical because of very large accompanying relaxation times. Practical values of q or q_e fall in the range of about 1.00 to 4.00. From the cases in which L, the length of the column, and ΔT, the temperature difference between the hot and cold walls, have been varied, it is seen that L and ΔT exert but a minor effect on separation efficiencies and relaxation times. The most important parameter is d, the wall spacing. Even a minute change in this parameter exerts a profound effect on the separation factors and relaxation times. Of lesser, but still significant, effect is the gravity level. This aspect of CDS is discussed further in Section 5.

Although the example cases are not strictly comparable, it is fairly evident that gases are most adaptable to CDS, allowing relatively large separations in relatively short time periods with relatively large wall spacings. Liquid metals probably have to be considered as least adaptable, especially with regard to wall spacings.

It is interesting to consider the results for UF_6 because of its historical importance. As mentioned earlier, CDS was first applied on a large scale in the separation of ^{235}U from ^{238}U. The uranium was in the form UF_6. The values of wall spacings and temperature difference (222°K), column length (1460 cm) in Case G3 are those which were used in producing ^{235}U by thermal diffusion during the war (Refs. 4 and 5). The separation factors achieved with such columns were on the order of 1.117 to 2.72. It is interesting to note, therefore, that present calculations show that the flow at a gravity level of 1g (980 cm/sec^2) in a 1460 cm long cell and 0.025 cm wall spacing across which 222°K is applied is turbulent. The numbers given in parentheses in Table 1 for this case are those calculated ignoring the condition that g should not exceed g_{opt} by ten. The present simple calculations, are of course, not strictly applicable to the real case, considerations such as cylindrical corrections and pressure having been ignored. The real case, however, oduced many puzzling features and inconsistencies (Ref. 6), arising undoubtedly from deviations from a strictly unicellular flow pattern. In Section 6 the effect of flow patterns on separation efficiency is considered further.

Another aspect of CDS that emerges from consideration of Table 1 is that sizeable separations of aqueous solutions are achievable with moderate temperature differences. The method, as a matter of fact, will probably find its greatest application in biological separations where molecules and ultramicroscopic particles to be separated are quite large, structurally complex and therefore possess large α factors. It may be worthwhile to mention that the absolute values of temperature can be as low as is practical from the viewpoint of freezing avoidance.

Furthermore, it can be seen from Table 1 that separation times for cells without reservoirs are quite short so that CDS for small scale laboratory or industrial applications should be very feasible.

Continuous Multistage Operation

Any production type CD cell would almost certainly be one which is continuously operated, i.e., unseparated solution would be fed in continuously at one point of the cell and product and stripped solution collected continuously at other points. Figure 2 illustrates schematically an arrangement for continuous CD operation

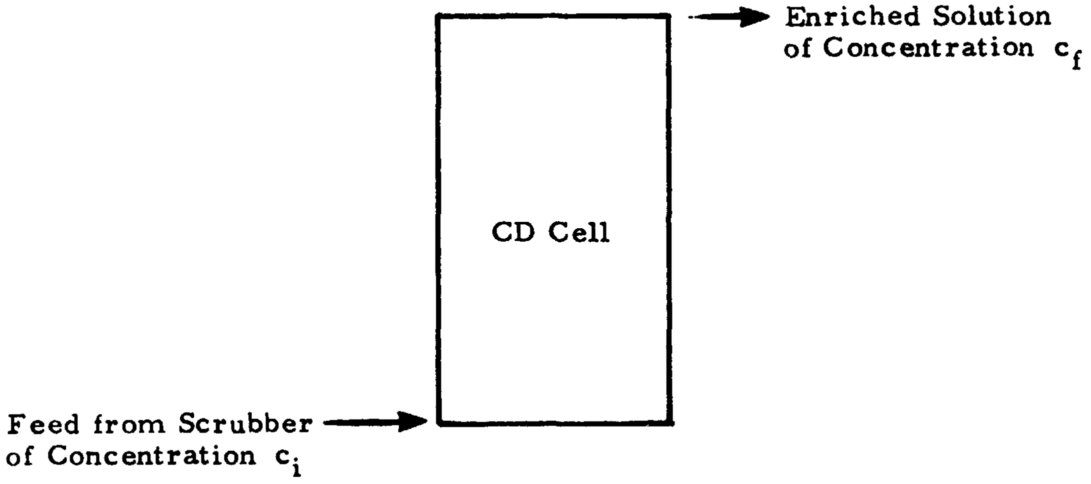


Fig. 2 - Schematic of a Continuous Single Stage CD Cell

A scrubber is an additional continous column run in the following fashion.

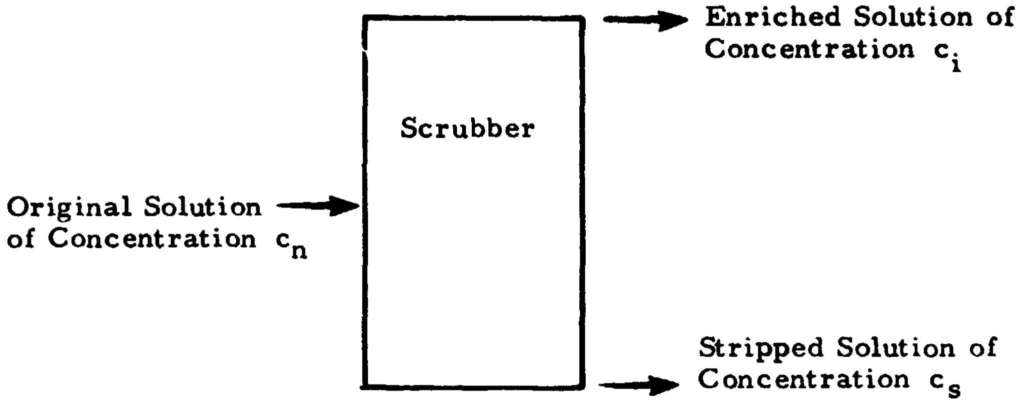


Fig. 3 - Schematic of a Scrubber CD Cell

Flow from the scrubber serves the purpose of maintaining the solution at the entry of the separating column at a constant concentration. It is usually desirable to adjust the rates of flow in the separation cell and in the scrubber so that the concentration at the entry of the separation column is the same as the concentration of the original solution, i.e., $c_i = c_n$. A more complete discussion of the details of scrubber design is given in Ref. 3. A sample calculation illustrating how a continuous rate affects separation is given in Appendix C.

From the viewpoint of multistage cell design the parameters of interest are σ/H and 2AL where σ is the flow rate in grams per sec and the other terms are as discussed in Appendix B. The term σ/H can be viewed as a yield factor and the term 2AL as a length factor. The quotient of the two terms, i.e.,

$$\frac{\sigma/H}{2AL} = \frac{\sigma K}{H^2 L} ,$$

is called the efficiency inasmuch as the cost of cell construction and operation is proportional to 2AL and the yield to σ/H. Obviously, the efficiency is the quantity to be maximized. In Ref. 3 tables of most efficient values of σ/H and

2AL for various q values are given. Furthermore, it is shown in Ref. 3 that. under widely varying conditions, the most effective value of 2AL is given by

$$2AL = 2 \ln q_e \quad \text{(two-log-q rule)}$$

In addition to being continuously operated most commercial CDSs are operated on the cascade or multistage principle for the twofold reason of increased capacity and separation. A simple cascade (Ref. 7) is sketched below.

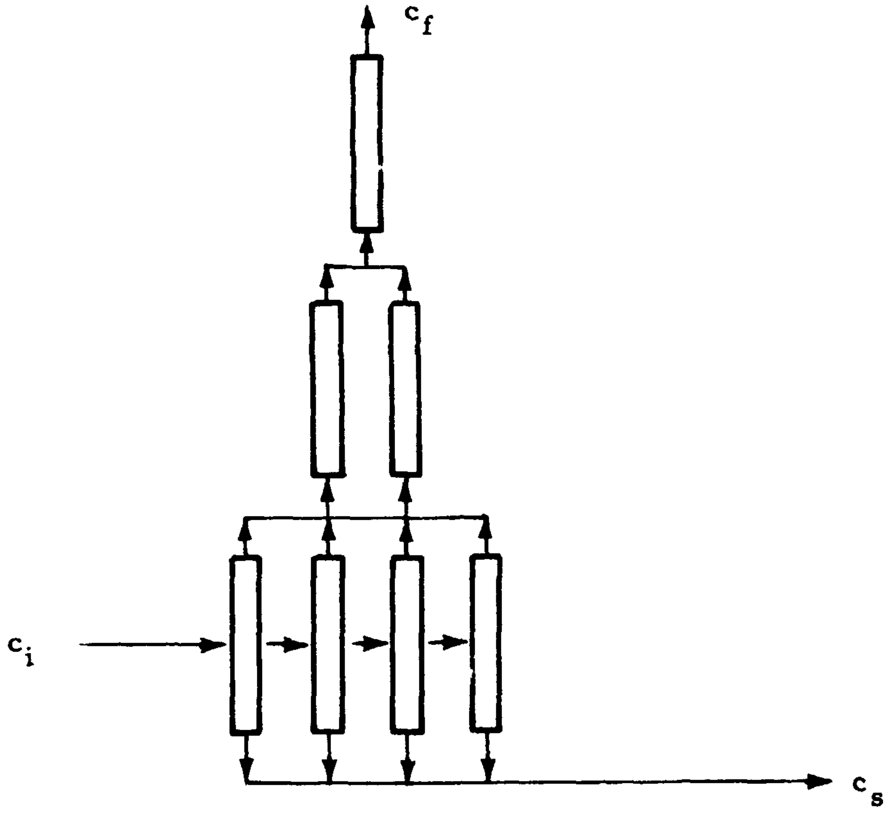


Fig. 4 - Schematic of a Simple Cascade (Ref. 7)

Much the same considerations as are discussed for single stage operation apply to the multistage case. The reader is referred to Ref. 3 for theory development. The points to be made here are that a cascade, assuming that all the cells are identical, can increase the separation factor and decrease the separation time compared to the same quantities for a single column. These effects are best illustrated by a simple example. Taking the case of sulfur (Case E3, Table 1), we have the following values of q_e and t'_r for a single cell

$$q_e = 1.56$$

$$t'_i = 24 \text{ days}$$

Suppose we set the production rate of enriched solution at one gram/day and the cascade construction at three stages beyond the scrubber, i.e., scrubber – 8 cells, first stage – 4 cells, second stage – 2 cells, third stage – 1 cell. A cell width (B) of 10 cm is further assumed (see Appendix B for discussion of influence of cell width in batch and continuous cells). Utilizing the relationship for most efficient multistage operation, (Ref. 3):

$$\ln q = A\mathcal{L} ,$$

where $\mathcal{L}$ is the total length of the cascade (not counting the scrubber) we obtain a separation factor of 1.95, i.e.,

$$\begin{aligned} \ln q &= 3.702 \times 10^{-3} \times 180 \\ &= 0.6664 \\ q &= 1.95 \end{aligned}$$

To obtain the characteristic time, i.e., the time before product can start to be withdrawn at a constant rate the following formula is applied.

$$t_c = 4\rho d B \frac{\sigma K}{\eta_1 H^3} \left[\frac{(c_i + c_f - 2\, c_i c_f) \ln q - 2\,(c_f - c_i)}{c_i\,(1 - c_i)} \right]$$

where η_1 is the number of cells in the first stage. For the conditions here defined t_c is calculated to be 1.7 days. Thus, separation can be increased from 1.56 to 1.95 and the separation times decreased from 24 to 1.7 days by utilizing a three stage cascade.

It is stated in Ref. 3 that for a separation factor of 10^5 the single-stage apparatus can have a characteristic time about 2000 times that of an ideal multistage apparatus. In practice a desired product concentration and production rate is specified and the cascade is then designed to optimize efficiency. One drawback of cascades is the expense of the hardware. Especially expensive is the construction of columns with the very narrow slit or annulus widths. One tremendous advantage of low-g operation would be the lower cost of hardware because wider slit or annulus widths could be utilized. This aspect of CD operation is discussed further in Section 6.

Power Requirements

As mentioned previously the large amounts of power required for CDSs of isotopes and petroleum fractions has been the chief deterent to commercial exploitation of the method. One experimental study of the efficiency of the method in petroleum separations (Ref. 8) reported experimental efficiencies of about 10^{-5}. The experimental efficiency, $\mathcal{E}_e$, is defined in the cited study by the following set of relationships

$$\mathcal{E}_e = \frac{\text{actual rate of separative work}}{\text{actual rate of heat input}}$$

$$= \frac{\sigma \Delta^2 R d \bar{T}}{8 \bar{M} c_1 c_2 \lambda L B (T_H - T_c)}$$

where

$$\Delta = c_e - c_s$$

and c_1 and c_2 are the mole fractions of components 1 and 2 in the original mixture, and σ is the rate of separation in grams per second. The other terms are defined in the notation section. The experimental efficiency $\mathcal{E}_e$ can be viewed as an energy conversion efficiency (Ref. 9, p. 192). As can be appreciated, actual conversion efficiencies of conventional CDS cells are quite low. Table 3 illustrates this point dramatically. In Table 3 the energy requirements per unit separative work (USW) per year for various methods for uranium isotope separation are given.

Table 3

COMPARISON OF ENERGY REQUIREMENTS FOR VARIOUS METHODS OF URANIUM ISOTOPE SEPARATION (Ref. 10)

Process	Specific Energy Consumption kw/kg USW/yr	
	Theoretical Minimum*	Practical
CDS with UF_6	61	
Gaseous Diffusion	0.073	0.266
Distillation		>0.62
Redox Ion Exchange		>0.71
Electromigration in $UC\ell_4$		1817
Molecular Distillation		>0.073
Isotope Chopper		>>0.073

*See Section 6 for discussion.

A USW as used in the preceding context is not work or energy but a term that indicates the degree of separation achieved, i.e.,

$$SW = W \left[\frac{c_e / [1 - c_e]}{c_s / [1 - c_s]} - 1 \right]^2 / 4$$

where W is one-half of the amount of feedstock. Furthermore,

$$SW = W\ V(c_e) + W\ V(c_s) - 2\ W\ V(c_f)$$

where c_f is the mole fraction of desired component in the feedstock and the V(c) functions are defined as

$$V(c) = (2c - 1) \ln(c/1 - c)$$

The units of SW are kilograms (Ref. 11). Thus, a SW of 4.306 kg/hr gives 1 kg/yr of 3% U^{235} from 5.479 kg/yr feedstock consisting of 0.711% U^{235} (Refs. 11 and 12).

Another study done in 1957 is of interest in connection with power requirements. Powers and Wilke (Ref. 13) estimated the costs and power requirements for processing 1000 bbl/day of 50 mole % n-heptane-benzene mixture to give products of 70% purity. Such a separation is indicative of separations involving aromatics and aliphatics and hence petroleum oils. The heat load for this apparatus design calls for 5.27×10^8 Btu/hr (5.56×10^{11} Joules/hr, 3.33×10^9 kilowatts). It is worthwhile to mention, however, that relatively low temperatures were assumed, i.e., $T_c = -8^oC$ and $T_H = 92^oC$.

The foregoing discussion of CDS efficiency has dealt primarily with the experimental or actual efficiencies achieved. The question of the limiting or thermodynamic efficiency is dealt with in Section 6.

Section 5
ADVANTAGES OF SPACE ENVIRONMENTS FOR CDS

Constant Low-g Values

In a spacecraft or on the surface of the moon steady low-g values are readily attained or already prevail. In a spacecraft the level of gravity desired can be achieved by controlled rotation, either of the spacecraft or of the apparatus in which the gravity is to be controlled.

Values of q_e, q, t_r' and t for various g levels are presented in Table 1. It can be seen that lowering g levels allows an increase in wall spacings by one to two orders of magnitude. To appreciate the practical advantage this fact affords, it will be well to reconsider the optimum wall spacings for separations at one-g. These are given in Table 4.

Table 4
SUMMARY OF WALL SPACINGS AT OPTIMUM G LEVEL OF ONE

System	d (cm)
Copper Sulfate	0.0154
Sugar in Water	0.0189
Cetane-Cumene	0.0092
Mercury	0.0074
Sulfur	0.2013
Methane	0.5271
Uranium Hexafluoride	0.01104

Powers and Wilkes (Ref. 13) set a wall spacing of 0.0793 cm as a practical design limit. Commercial laboratory cells (see Appendix E) are available with wall spacings down to 0.01 cm. However, a comparison of the work of various investigators (Ref. 14) in which d ranged from about 0.6 to to about 0.04 cm reveals conflicting results and large deviations from theory. In further study of the effect of cell variables on performance it was concluded that the descrepancies probably arose in the critical nature of the wall spacing (Ref. 14). Other instances of anomalous or puzzling results can be cited (Refs. 4 and 15) which also undoubtedly have their origins in small variations in the wall spacing. The present study also noted an anomolous result at wall spacing of 0.01 cm (Appendix E). Small wall spacings have the further disadvantage of smaller processing volumes. Obviously, if the wall spacing can be increased in low-g, small wall imperfections will have less effect. More reliable cell performance and larger processing volumes will be possible as a result.

The beneficial effects of reducing gravity on cell performance have been noted previously. In one study (Ref. 13) a flat plate cell was tilted so that the force of gravity could be reduced according to the relationship $g = g_g \cos\theta$ where θ is the angle between the cell and the gravity vector, i.e.,

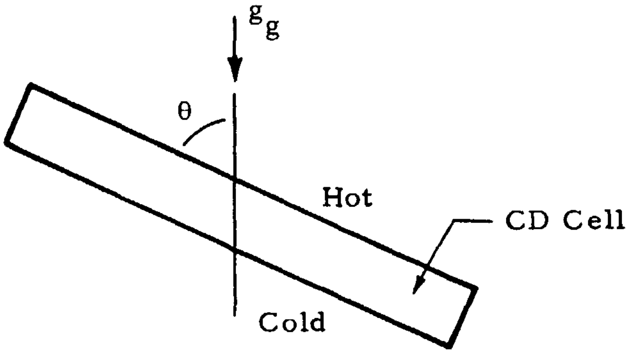


Fig. 5 - Tilted Flat Plate Cell

Whether the full benefit of reduced gravity can be realized from this arrangement is doubtful because studies currently in progress show that a layer of fluid can be tilted only so far. Further tilting results in a breakdown of the unicellular flow pattern into a multicellular one. The question of flow pattern however, is considered further in Section 6. Also, gravity stresses on the cell as a whole would have a deleterious effect on maintenance of the critical wall spacing.

In a number of other studies (Refs. 16 through 25) CD cells were packed with various packings such as glass wool, metal turning, etc. Such cells showed impressive separation at relatively large wall spacings. It was generally concluded that the increased separation resulted from a decreased convective velocity. However, the space taken up by the packing and the generally larger times to reach a given level of separation generally cancelled the larger wall spacing benefit. It should be noted that packing offers an immense advantage for small batch or laboratory separations. Fairly crude cells can be used. For example, a 3% copper sulfate solution could not be separated in an unpacked cylindrical cell made of glass (0.721 cm annulus, Case A1, Table 1). Essentially complete separation, however, occurred in about four hours when the column was packed with glass wool. No special materials or procedures were utilized to ensure that cell annulus spacing was precise. Cell variation and misalignment were undoubtedly great. Appendix E gives the experimental details for this and other separations performed during the present study.

In summary, a space environment offers all of the advantages of convective velocity reduction with none of the disadvantages noted for reduced convection operation on the ground.

In addition to the foregoing advantages the further advantage of alleviating the "forgotten effect" will be realized at low-g levels. The "forgotten effect" occurs when the components of the solution are such that the density of the solution concentrating at the hot wall becomes greater than surrounding fluid. An overturning as remixing of the solution eventually occurs. In low-g environment greater concentration can be achieved before the overturning occurs.

Gravity Gradient

Control over gravity levels in a space orbital environment will be achieved either by spacecraft rotation or cell rotation. In such situations the further option exists of having a sizeable gravity gradient. Consider the gravity gradient shown on the following page:

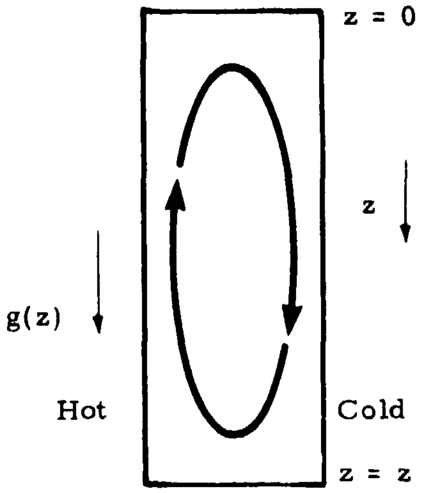


Fig. 6 - Schematic Showing One Possible Direction of a Gravity Gradient

The convective flow inside the CD cell would certainly be different than if the gravity level were independent of column height. In the posed situation, the heat flow would encounter lesser gravity as it rises, and the cold flow would encounter greater gravity as it falls. A mathematical analysis for CDS in a cell subjected to considerable gravity gradient does not exist at present. It is not possible, therefore, to evaluate gravity gradient effects realistically. A speculation, however, may be offered. The following equation is given for heat transfer from an isothermal vertical plate, i.e., Fig. 7, in the presence of a gravity gradient (Ref. 26):

$$\frac{Nu}{\overline{Nu}} = 1 + \frac{7}{24}\,\frac{bx}{a}$$

where Nu is the Nusselt number in the presence of the gravity gradient, $\overline{Nu}$ the Nusselt number in the absence of a gravity gradient, b the gravity gradient at x, and a the gravity level at x = 0. Depending on the values of a, b and x, Nu can be greater or less than $\overline{Nu}$. If Nu is less than $\overline{Nu}$, convective velocities

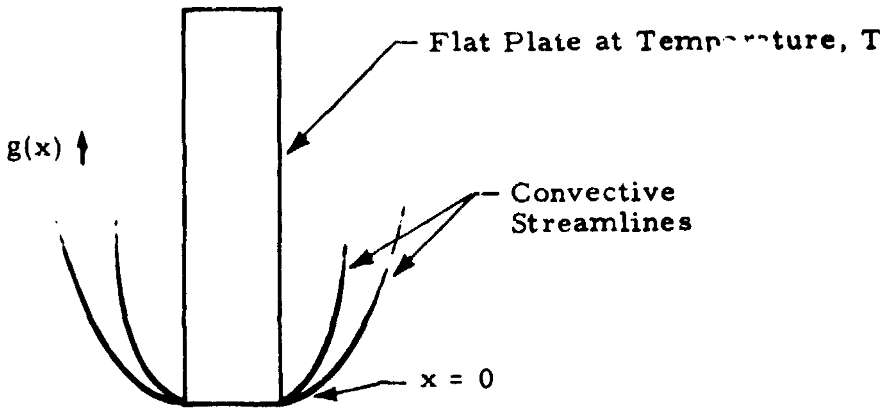


Fig. 7 - Schematic of Gravity Gradient Situation Analyzed by Catton (Ref. 26)

are obviously reduced as the result of a gravity gradient. Thus, one use of a gravity gradient may be to move onset of turbulence to gravity levels greater the 10 x g_{opt}, allowing cell operations at gravity levels greater than 10 x g_{opt}. It will be recalled that operation at ~10 x g_{opt} gives greatest efficiency, i.e., most separation work in the shortest period of time. Presumably, even greater efficiency would accrue at values greater than 10 x g_{opt} if turbulence could be avoided. Whether such a possibility is realistic, however, requires more detailed consideration of the operational mathematics.

Utilization of a gravity gradient in one-g, though possible, would appear to be a complicated affair, necessitating vibration free mountings, special electrical connections, etc. Rotation of a spacecraft or of a cell in space, on the other hand, appears relatively easy.

Solar Heating and Outer Space Cooling

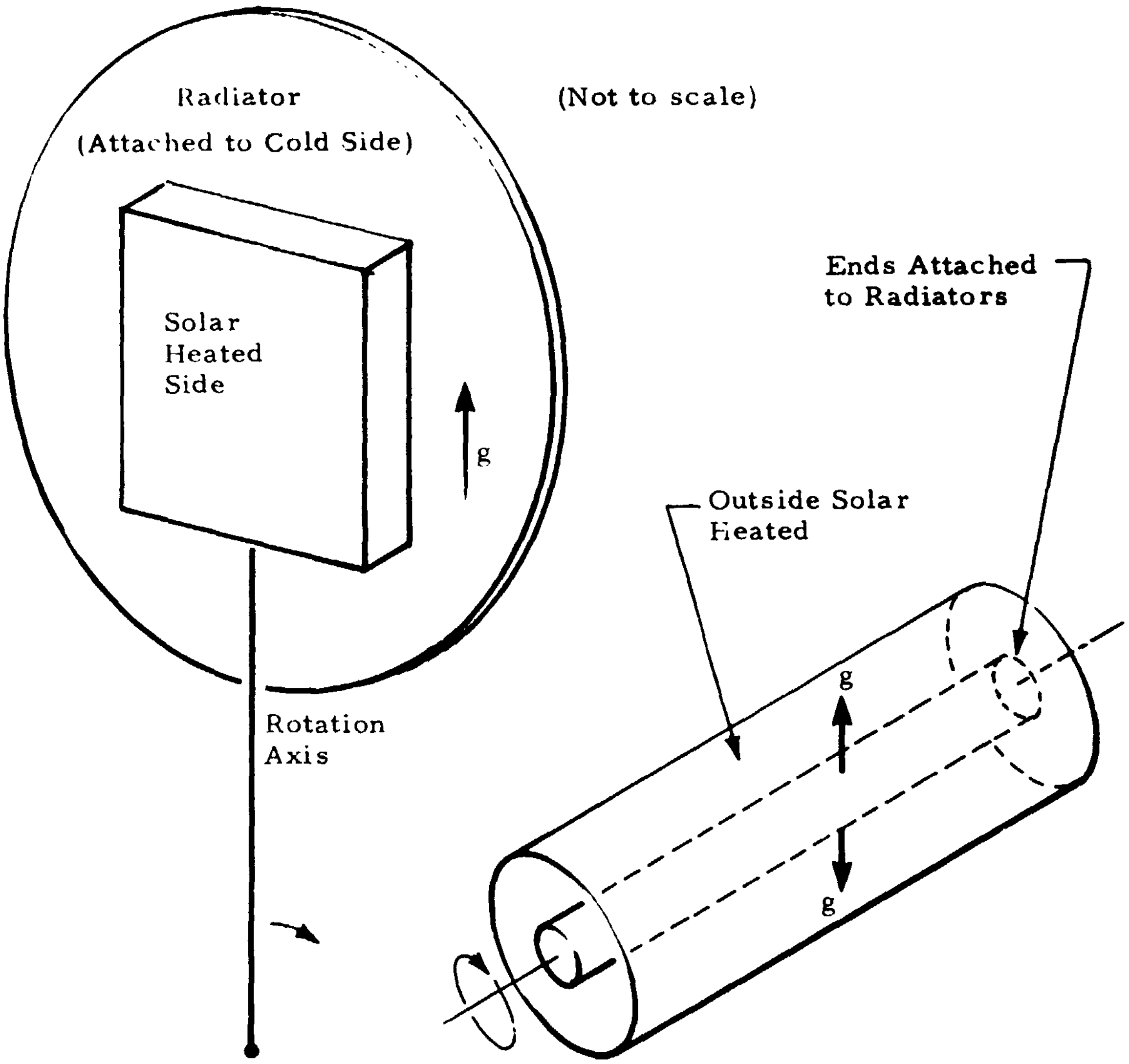
On earth the power requirements for commercially processing sizable amounts of materials in a CD column are huge and expensive, especially in cases of isotope separations. The idea of utilizing solar energy to heat one surface of a CD column and the blackness of outer space to cool the other, therefore, promises a real low-g benefit. A couple of likely concepts for accomplishing solar heating and outer space cooling is shown in Fig. 8. Whether the situation depicted in (b) in Fig. 8 is desirable for separations is undecided at present. See Section 6 for further discussion.

With ingenuity as to the arrangement and size of focusing parabolic mirrors, a variety of temperature ranges and cell configurations can be achieved. In earth orbit the solar energy intensity is of the order of 0.14 W/cm^2 or 2 cal/cm^2-min. (Ref. 27). This amount of heat would raise the temperature of a cubic centimeter volume of water 2°C in one minute. The assumed thermal conditions shown in Fig. 9 for the separation of aqueous solutions in a rectangular cell of the dimensions and materials indicated would require a 2.32 fold concentration of natural solar radiation. Such a level of solar energy concentration would require a parabolic concentrator of 2.7 square meters in area. A large concentrator in space should present no major problem for without gravity stress aluminized plastic umbrella collectors can be utilized. Design of a thermal radiator to dissipate the 0.075 cal/sec-cm^2 required to maintain a 50°C temperature gradient will present more of a problem but not an unsolvable one.

Radiation Effects

It is well known that the various radiations encountered in space environments can produce pronounced effects on materials. One, of course, would not suggest going to space just to utilize the radiation environment. However, if one is contemplating conducting CDS in space, it is a reasonable question to ask what further advantages might result from radiation exposure.

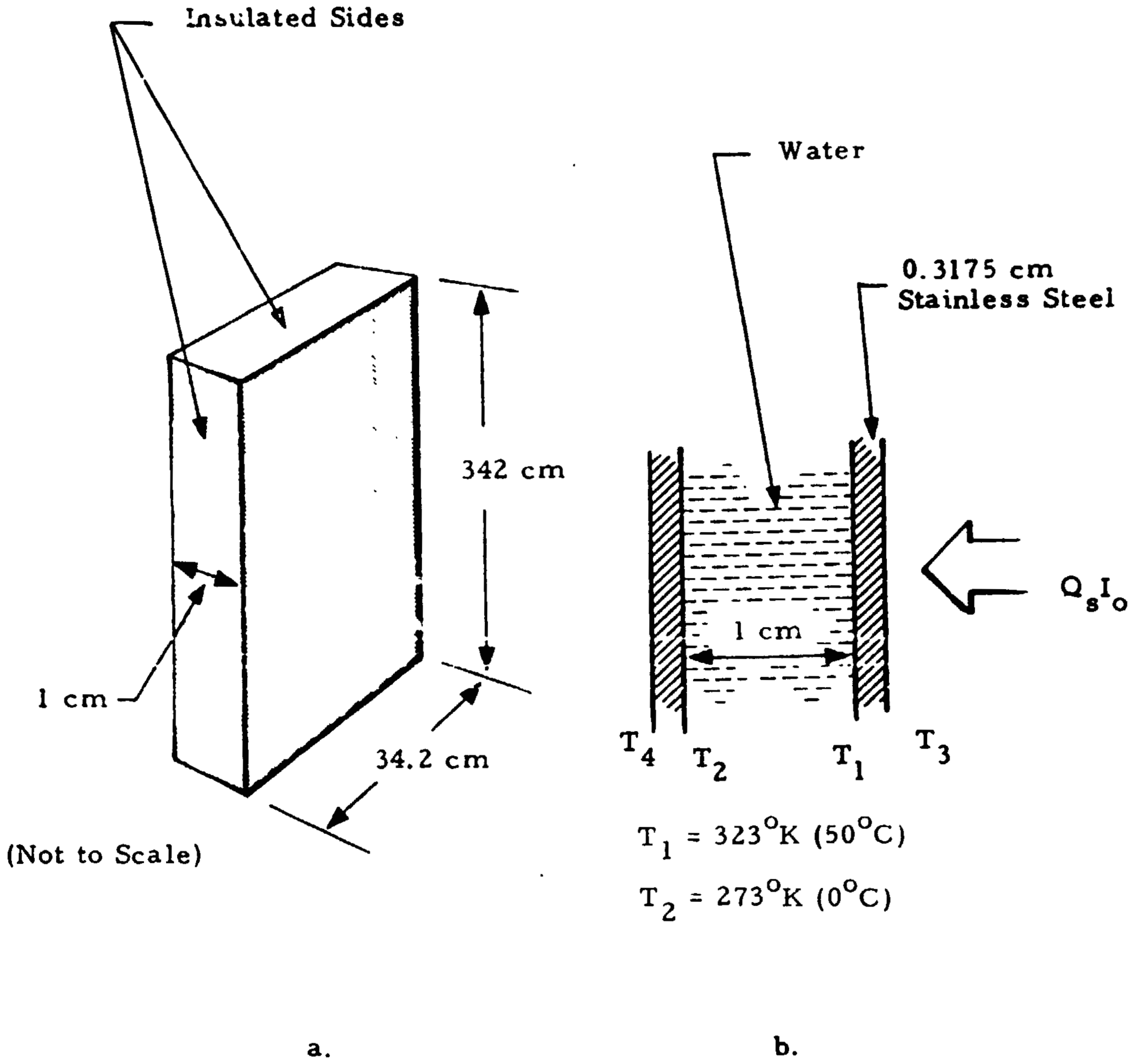
Two material areas suggest themselves for further investigation. The first involves radioisotope production by both CDS and radiation and the second chemical synthesis and subsequent purification. Upon radiation with certain energy nuclear particles or electromagnetic waves, a nucleus can be converted



a. Flat Plate Cell

b. Cylindrical Cell (The heating/cooling arrangement could just as well be switched, i.e., outer surface cooled, inner cylinder heated).

Fig. 8 - Concepts for Utilization of Solar Heating and Space Radiation Cooling for CDS



k_{Water} = 0.0015 cal/sec cm^2 °C/cm

$k_{Stainless\ Steel}$ = 0.1 cal/sec cm^2 °C/cm

ϵ_3 (emissivity) = 0.0

ϵ_4 = 1.0

α_1 (absorbtivity) = 1.0

Fig. 9 - Cell Assumed for Sample Calculation of Required Solar Energy Concentration for Separations of Aqueous Solutions; (a) overall dimensions, (b) detailed cross section

into either a stable or a radioactive isotope. For example, ^{46}Ca irradiated with neutrons produces radioactive ^{47}Ca and gamma rays. ^{47}Ca is useful by itself for base metabolism studies or for production of radioactive ^{47}Sc. The usual procedure for producing ^{46}Ca is by enriching a mixture of natural isotopes. ^{46}Ca exists in natural mixture at 0.0033% weight concentration. The natural mixture is enriched to levels of 25 to 47%. At the 40 to 47% level ^{46}Ca sells for $880/mg (Ref. 28). The enriched isotope mixture is then bombarded with neutrons to produce ^{47}Ca. ^{47}Ca can be further bombarded with beta particles to produce ^{47}Sc. A mixture of the various Ca and Sc isotopes with a specific activity of 1000 mCi/g Ca is currently worth $250,000 (Ref. 28).

For space operation a process can be conceived whereby a CDS operation enriches a natural mixture of Ca isotopes with the ^{46}Ca member. The enriched mixture would then be subjected to neutron radiation which is generated either by proton space radiation impinging directly on a target or by neutron radiation produced by a device such as a linear accelerator which would be run on solar energy. The magnitudes of various radiations likely to be encountered in earth orbit are indicated in Table 5.

Table 5

MAGNITUDES OF VARIOUS RADIATIONS NEAR THE EARTH (Ref. 27)

Radiation and Energy	Earth Orbit Flux (particles/cm^2-sec)
Protons	
0.4 MeV	10^3 - 19^8
4.0 MeV	10 - 10^6
34.0 MeV	10 - 10^4
Electrons	
>0.5 MeV	10^2 - 10^8
Alpha Particles	

$$\frac{\text{Flux of Alpha Particles with Energy} > 2.09 \text{ MEV}}{\text{Flux of Protons with Energy} > 0.52 \text{ MEV}} = 2.3 \times 10^{-4}$$

The fluxes indicated in Table 5 are substantially lower than those produced by nuclear reactors and particle generators such as the Oak Ridge 86-inch cyclotron. The cyclotron can produce a 17 MeV proton flux of 7.8 x 10^6 particles cm^2-sec (Ref. 29). To simulate the radiation of 23 MeV in the Van Allen belt the cyclotron was run at a 3 particles/cm^2sec flux density (Ref. 29). Exposure to cyclotron radiation, however, are usually quite short, on the order of a few minutes. The cyclotron and other devices producing radiation on earth, moreover, consume enormous amounts of energy. The cyclotron, for example, uses a 1500 amp current to energize a 400 ton magnet, and a 4300 amp current for a magnetic deflection coil. Additional power is further required for cooling and proton production. The Oak Ridge research reactor which can produce a neutron flux of 1.6 x 10^4 neutrons/cm^2-sec consumes 30 MW operating power (Ref. 30). It can be appreciated that radiation treatments on earth can be costly.

Although earth reactors can achieve higher fluxes than are likely to be achieved in space, space fluxes are sufficient to produce usable amounts of radioactive isotopes because longer exposure times can be used. Once in space the radiation is "free" for as long as we choose.

The advantage of space radiation in a second area of possible application (the chemical synthesis and subsequent purification) conceivably could lie in the fact that low levels of radiation for long periods of time can be easily obtained in space. Past research has shown that some free-radical type chemical processes depend on the dose rate in an inefficient way: as the dose rate is increased the yield of product per 100 eV unit of radiation decreases. The proposed solution to this problem (Ref 31) is increased radiation time, area, or volume. The proposed solution is equivalent to decreasing flux density which can easily be accomplished in space. The proposed solution in earth operation would result in increased cost for equipment and holdup time.

It may be mentioned that investigation of radiation on the ground has found few important product areas. Specialty isotopes for medical and tracer activities, and uranium and plutonium for energy production, and nuclear weapons constitute the chief product areas. Activities such as food processing and chemical synthesis have proved uneconomical for a variety of reasons but an important one is the cost of radiation (Ref. 31). The cost of radiation since Ref. 31, used as the chief source in this report, was written in 1959 has undoubtedly skyrocketed. The idea of going to space to perform CDS in conjunction with radiation treatment, therefore, might for some processes present attractive advantages.

Section 6

THE QUESTION OF CDS EFFICIENCY IMPROVEMENT BY AN ORDER OF MAGNITUDE OR MORE BY ALTERED CONVECTION

The question of whether CDS efficiency, i.e., separation level achieved per unit of heat input, can be boosted by an order of magnitude or more is one that has intrigued and employed the energies of a number of investigators. In the period 1939-1955 a minor controversy existed on whether turbulence or flow patterns other than unicellular could increase substantially the separation efficiency of CD cells (Ref. 3, pp. 219-220 and Refs. 6, 32-37. A number of experimental studies in the cited references reported substantial increases in separation levels as the result of column design alterations such as packings, barriers, baffles, or spacers. The question of efficiencies, however, was never resolved conclusively, i.e., it was never demonstrated conclusively that the modifications could achieve a substantially higher level of separation of a given amount of mixture in a shorter time. Before proceeding it will be well to review the theoretical definition of the limiting thermodynamic separation efficiency. This was derived by Onsager (Ref. 38). Onsager's thermodynamic efficiency for any small volume of mixture consists of the following ratio:

$$S_o = \frac{\text{rate of decrease in entropy due to separation}}{\text{rate of increase in entropy due to heat conduction}}$$

By appropriately incorporating the transport rates by thermal and ordinary diffusion, Onsager obtained the following limits for S_o:

$$S_o \leq \frac{1}{4} \alpha^2 c_1 c_2 \frac{P D_{12}}{\lambda T} \qquad \text{(for gases)}$$

In energy terms the relationship is (Ref. 9)

$$\mathcal{E}_o \leq \frac{\alpha^2 D_{12} c_1 c_2 R(T_H - T_C) \bar{\rho}}{4\bar{M} \lambda \bar{T}} \qquad \text{(for gases or liquids)}$$

where c_1 and c_2 are the mole fractions in the unseparated mixture. Equality obtains when

$$J_{D'} = 2\, J_{D_{12}}$$

that is when the flux due to thermal diffusion is twice the ordinary diffusion. It may be well to mention that the entropy efficiency goes to zero at infinite time, i.e., at equilibrium or steady state no more separation work is being performed.

Jones and Furry (Ref. 3, pp. 198-199) determined the entropy ratio for an ideal, conventional CD cell (no asymmetries or imperfections), assuming that the product $c_1\, c_2$ varies little along the cell, and showed that an ideal conventional CD cell would operate at about 70% of the Onsager efficiency. They noted that a maximum Onsager efficiency would be approached only once during a separation, at the time

$$t = t_r' \ln 2 \, .$$

The average efficiency theoretically achievable is discussed further by Jones and Furry in Ref. 3.

White and Fellows (Ref. 9) determined the experimental efficiencies of single CD cells separating petroleum type mixtures and showed that they were of the same order of magnitude as the thermodynamic limiting efficiecies. Furthermore, they concluded that the experimental efficiency of a "constant separation" cascade would be the same as for one single cell in the cascade.

Consideration of the preceding information leads to the conclusion that if the thermodynamic efficiency of a CD separation is increased because of altered flow pattern, it can only be the result of (a) introduction of a sizable c_1, c_2 variations along the column, or (b) introduction of another separation mechanism (in addition to thermal diffusion) or (c) both. The Onsager thermodynamic efficiency, it will be recalled, depends on the product of the mole fractions c_1 and c_2. The product varies most in the range where c_1 or c_2 are less than about 0.3. In the range 0.3 to 0.7 the product $c_1 \cdot c_2$ is virtually constant.

One possible flow pattern which might vary the concentration appreciably along a cell is sketched below:

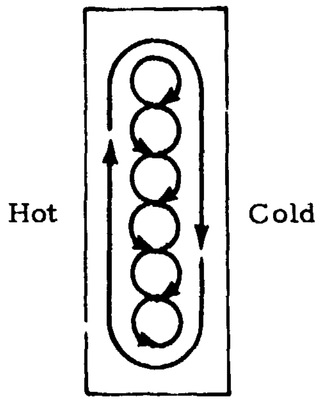


Fig. 10 - Schematic of an Internal Cascade

Cascading can have an appreciable effect on boosting separation levels, as previously discussed. The multicellular pattern shown in addition to providing a cascading mechanism may also be capable of sustaining internal, dynamic pressure gradients of sufficient magnitude to allow some significant pressure diffusion. Pressure diffusion is the phenomenon of separation by means of a pressure gradient, analogous to thermal diffusion in which separation is achieved by a temperature gradient. Pressure diffusion is usually not considered unless sizable pressure gradients such as generated by centrifuging are involved. The contribution of pressure diffusion coupled with thermal diffusion in a sustained convection field, however, may possibly be significant. For example, Chapman (Ref. 39) notes that for equal values of $\ln P/P'$ and $\ln T'/T$ pressure diffusion is from 2.5 to 3.2 times more powerful as a separating force than thermal diffusion. Consider the hydrostatic pressure at the bottom of a 100 cm long column of water. This would be given by the following formula:

$$P = P'_{(1\ \mathrm{atm})} + \rho g h = 1.098\ \mathrm{atm}$$

Therefore,

$$\ln \frac{1.098}{1} = 0.0934$$

and

$$\ln \frac{T'}{273^{\circ}\mathrm{K}} = 3 \times 0.0934$$

$$T' = 361^{\circ}\mathrm{K}$$

$$T' - T = 88.3^{\circ}\mathrm{C} \text{ or } {}^{\circ}\mathrm{K}$$

In other words a column of water 100 cm high in a gravitational field has the same separating power as a temperature difference of 88.3°C. A temperature gradient of 88°C is a substantial separating force in aqueous solutions when coupled with a convective field. The expectation of some significant pressure diffusion separation in CDS as the result of coupled hydrostatic and dynamic pressure gradients, therefore, may not be too unrealistic. One experimental test of the possibility that small pressure gradients coupled with sustained flow would increase separation efficiency was conducted in the course of the present study. As part of an experimental plan to determine practical problems involved with various type CD cells and to test the effect of multicells on separation efficiency a rotated column was constructed (Appendix E). At slow rotation rates the basic nature of the unicellular flow would not be disturbed. The small pressure gradients, however, would be. Results of tests at slow rotations, equivalent to g levels in the range of about $10^{-3}\ g_g$, indicate that small pressure gradients perpendicular to the earth gravity hydrostatic pressure gradient apparently can affect separation efficiency (Appendix E). More conclusive data, however, are required.

The present study attempted to verify experimentally that separation efficiency could be increased by introduction of a multicellular flow pattern. The impetus for this work was occasioned by the relatively recent work of Elde

(Ref. 40). Elder found that depending on the magnitudes of three dimensionless parameters three convective regimes are possible in a long, thin slab of fluid. The three-dimensionless parameters are Pr, the Prandtl number ($=\nu/k$), A, the aspect ratio (= length of cell/thickness of cell), and Ra, the Rayleigh number ($= \beta g \Delta T d^3/\nu k$). For large aspect ratios in the range of about 60 and Prandtl numbers of about 10^3 (oils) the following general flow patterns were observed.

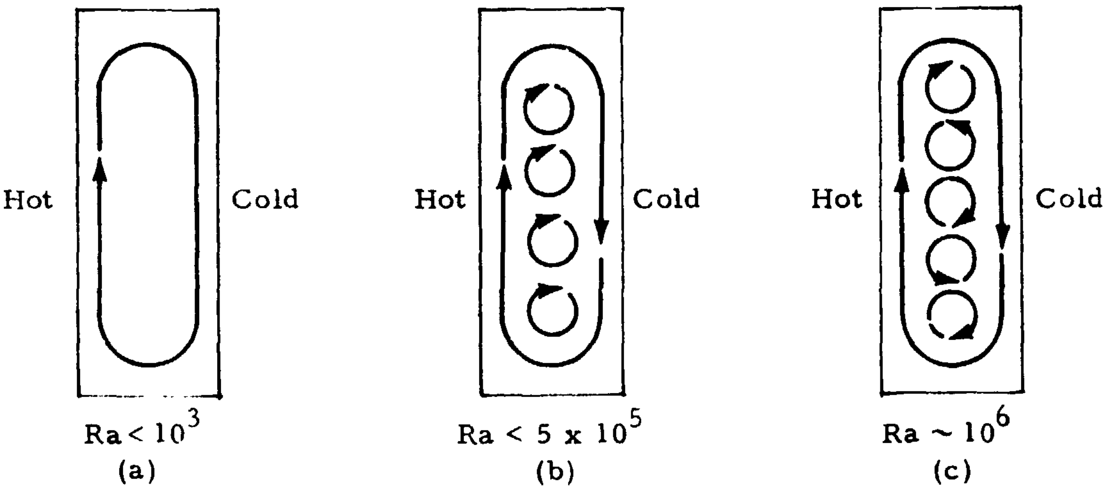


Fig. 11 - Flow Patterns in a Thin Slab as a Function of Rayleigh Number

Cohen (Ref. 6, p. 13) briefly considered the effect of the following cellular flow on separation.

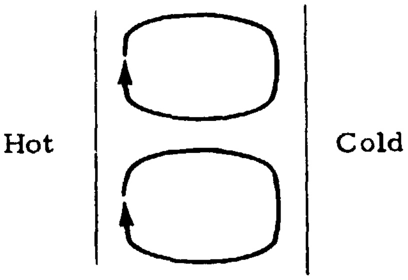


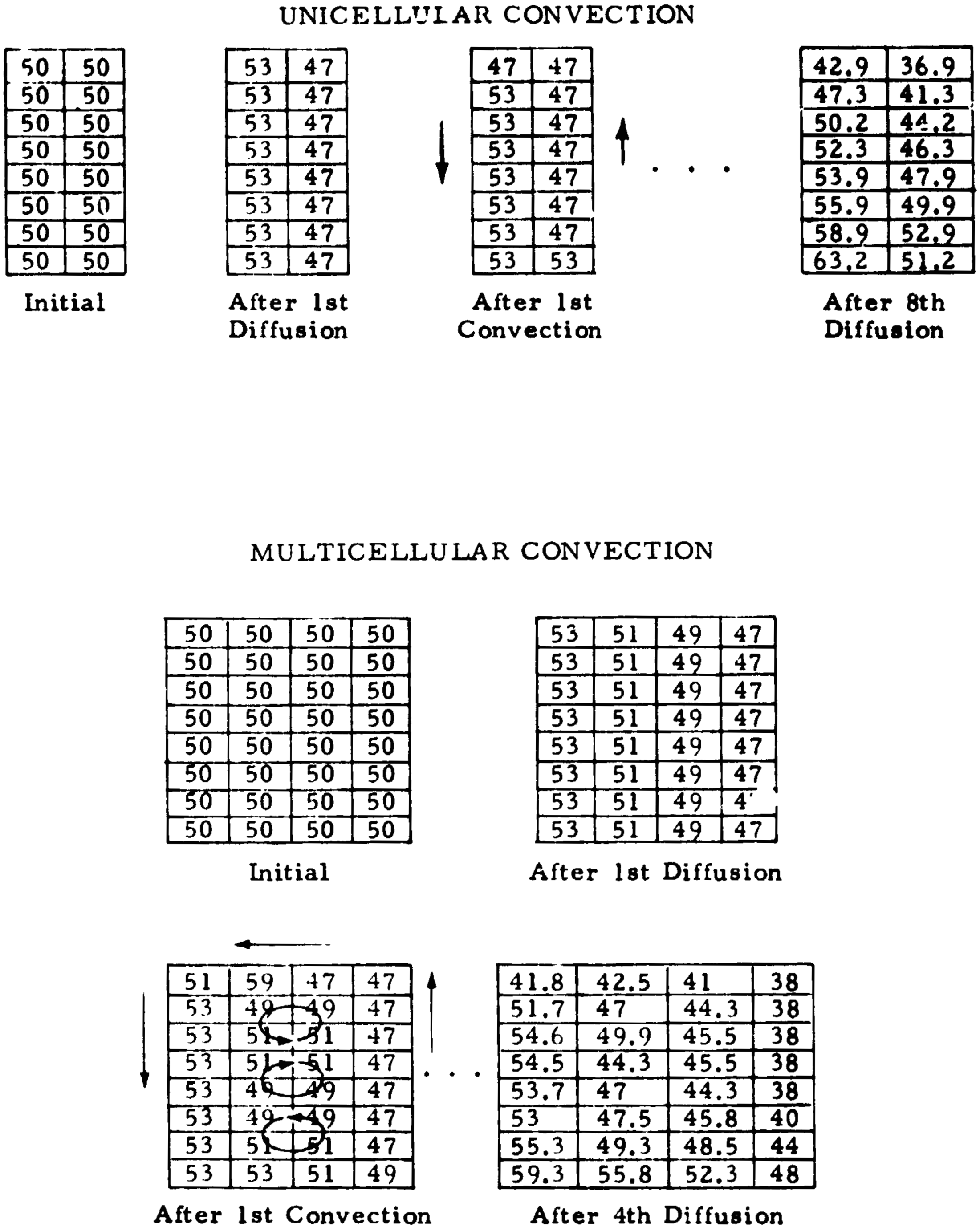
Fig. 12 - Cellular Pattern Postulated by Cohen (Ref. 6)

Cohen concluded that such a flow would seriously decrease separation. The present author agrees. The effect of such a flow coupled with an overall unicellular flow as is shown in Fig. 11b., however, is not obvious. The result of a flow pattern such as shown in Fig. 11c is also not obvious.

The results of the present experimental work of multicellular efficiency on separation efficiency are unfortunately inconclusive because of the difficulties encountered in generating multicellular flow in aqueous solutions. The conditions for generating multicells in low Prandtl number fluids, i.e., aqueous solutions are apparently not the same as for high Prandtl numbers. Further details are given in Appendix E. (See discussion in Flat Plate Cells.)

Although experimental verification of multicell efficiency was not achieved in the present study, a "numbers game" given in Fig. 13 (first introduced by Grew and Ibbs (Ref. 41, p. 92)) to illustrate the principle of CDS provides further support for the expectation that multicells can improve CD efficiency.

In connection with improving CDS efficiency and also in connection with CDS operations in low-g environments, it was of interest to seek an answer for the question of how rotation might affect separation. (In a space environment cell rotation can easily be accomplished). Although a number of previous studies (Refs. 42 through 45) have reported improved separation as the result of rotating either an entire CD column or only one wall (i.e., either the inner or outer cylinder would be rotated while the other remained stationary), the efficiencies obtained are obscure. Especially intriguing, however, is the work of Sullivan, Ruppel, and Willingham (Ref. 45) because multicells or spirals apparently did play a major role in their separations. These workers used a conventional vertical cylindrical column, but the inner cylinder was rotated in some of the experiments. Definite increases of separation up to a factor of about 10 were observed. Sullivan et al., noted in their rotated cells "moving spirals which have a secondary motion that gives them the appearance of a coil .... at optimum speed the motion of the liquid is in the form of layers of rings with each resembling two circular coils wrapped in opposite directions." A space



UNICELLULAR CONVECTION

50	50
50	50
50	50
50	50
50	50
50	50
50	50
50	50

Initial

53	47
53	47
53	47
53	47
53	47
53	47
53	47
53	47

After 1st Diffusion

47	47
53	47
53	47
53	47
53	47
53	47
53	47
53	53

After 1st Convection

. . .

42.9	36.9
47.3	41.3
50.2	44.2
52.3	46.3
53.9	47.9
55.9	49.9
58.9	52.9
63.2	51.2

After 8th Diffusion

MULTICELLULAR CONVECTION

50	50	50	50
50	50	50	50
50	50	50	50
50	50	50	50
50	50	50	50
50	50	50	50
50	50	50	50
50	50	50	50

Initial

53	51	49	47
53	51	49	47
53	51	49	47
53	51	49	47
53	51	49	47
53	51	49	47
53	51	49	4[illegible]
53	51	49	47

After 1st Diffusion

51	59	47	47
53	49	49	47
53	51	51	47
53	51	51	47
53	49	49	47
53	49	49	47
53	51	51	47
53	53	51	49

After 1st Convection

. . .

41.8	42.5	41	38
51.7	47	44.3	38
54.6	49.9	45.5	38
54.5	44.3	45.5	38
53.7	47	44.3	38
53	47.5	45.8	40
55.3	49.3	48.5	44
59.3	55.8	52.3	48

After 4th Diffusion

Fig. 13 - Schematic After Grew and Ibbs (Ref. 41) Illustration of Concentration Changes in a CD Cell with Unicellular and with Multicellular Convection: A 6% Separation as the Result of Thermal Diffusion is Assumed

of "clear, apparently motionless fluid" in between both spiral flows was observed. It is also interesting to note that in two previous studies in which the inner cylinder of a CD column was wrapped with a spiral wire (Refs. 46 and 47a) higher levels of separation and greater rates of separation were reported. Efficiency improvements, however, were not conclusively established.

In space it would be more desirable to rotate the whole column rather than just one wall. A spiraling flow, however, can be generated in an apparatus in which both cylinders are rigidly connected and rotated around their common vertical axes, while either a positive or negative radial temperature difference is maintained between both cylinders.* A thorough numerical investigation of such flows has been made by Williams (Ref. 47b). Essential features of Williams' computations have been confirmed experimentally by Koschmieder (Ref. 47c). It was found in these experiments that the centrifugal force has a substantial effect on the circulation in the annulus. The transition to a three-dimensional vortex flow was found to depend strongly on whether the thermal circulation was either parallel or opposite to the centrifugal circulation which moves warm light fluid inward and cold heavy fluid outward, just as in a centrifuge.

The original intent of the present study was to experimentally investigate the effect of centrifugially generated spirals on separation. Development of apparatus and procedures, however, were more involved than anticipated (Appendix E), so this part of the study must necessarily be postponed for the future.

To summarize, it appears that a reasonable case for improvement of CDS efficiency by means of flow pattern alteration can be made. The matter certainly warrants further study because of its possible impact on reducing the energy requirements for uranium isotope separation. Various methods for separating uranium isotopes are currently being intensively investigated because of the urgent energy crisis situation. Conventional CDS, however,

---

*If the inner cylinder is cold and the outer hot, the temperature gradient is positive. If the reverse is true, the temperature gradient is negative.

was dismissed a long time ago, as being too energy costly. The matter is important also from the viewpoint of space processing. Although unlimited "free" solar energy will be available in space which can be readily collected, maintaining a cold wall by radiation to outer space will be more difficult. Obviously, any improvements in separation efficieny would be advantageous.

Section 7
CDS VARIATIONS AND ALLIED TECHNIQUES

In the preceding section improvement of CDS efficiency by means of convective flow pattern alteration was considered. In this section some CDS variations and allied techniques will be discussed.

Electrophoresis-Convection and CDS Plus Electrophoresis

The technique of electrophoretic separations is quite similar to separation by a temperature gradient. As a matter of fact, the idea of coupling the two driving forces was proposed as a method of determining Soret coefficients (Ref. 48). Most practical electrophoresis separations are conducted in the absence of convection. Electrophoresis coupled with a forced, laminar convective flow, however, is also utilized. The ideal of coupling CDS and electrophoresis was inevitable. Crosser, Powers, and Prabhudesai (Ref. 49) report the results of a study in which the apparatus utilized had the following essentials:

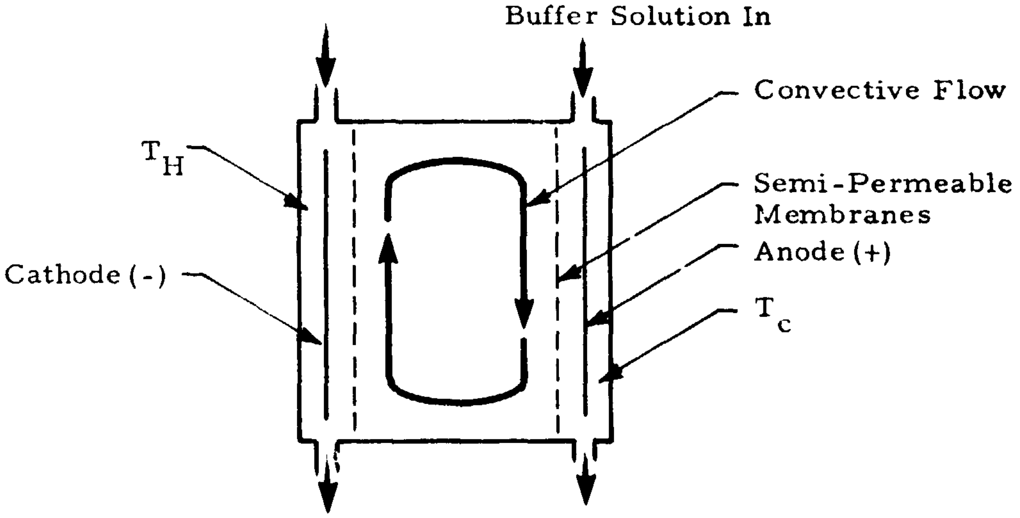


Fig. 14 - Essentials of a Electrothermogravitational Electrophoresis Column

It can be appreciated that with such a relatively complicated system that it will take more than the first reported studies to adequately determine the potential of the technique. The first study reports unsurprisingly a number of problems. Much of the difficulty in obtaining agreement between theory and experiment appears to be the result of the large cell spacings used in the experimental work. Such difficulty suggests that this technique also will profit from low-g processing.

The material system used in the cited experimental study was a bovine albumin system. The technique probably would be easier to develop using systems such as aqueous electrolyte solutions, liquid metal solutions, or molten salt solutions. Each of these latter systems is capable of conducting electricity and therefore is a suitable candidate for separation by this technique. Possibly the technique also may eventually be suitable for isotope separations. Big questions about the technique remain to be answered, especially the question of efficiency.

CDS Coupled with Chemical Reaction

A few studies were done in this area in the 1940s and 1950s. As far as is known, no further studies have been since accomplished. The coupling of chemical reactions with CDS can be a means to accomplish some unique separations. For example, oxygen isotopes occur naturally as mixed molecules, i.e., $O^{18}O^{16}$. At a hot surface, however, the following reaction occurs (Ref. 1)

$$2O^{18}O^{16} \rightleftharpoons O_2^{16} + O_2^{18}$$

The separating effect of CD drives the equilibrium toward the right, with the result that practically pure O_2^{18} is obtained at one end. Other separations reported include C^{13} by the exchange reaction (Ref. 50)

$$C^{12}O_2 + C^{13}O \rightleftharpoons C^{13}O_2 + C^{12}O$$

and N^{15} by the exchange reation (Ref. 51)

$$N^{14}O_2 + N^{15}O \rightleftharpoons N^{15}O_2 + N^{14}O$$

As a method of separating isotopes, however, apparently not much advantage is realized over CDS without chemical exchange (Refs. 49 and 50).

Hirota and Kimuro (Refs. 52 through 55) carried out hydrogenation and polymerization reactions of acetylene and of methane. A desulfurization reaction was also reported as having been studied (Ref. 54). CDS was used in these studies to prevent decomposition of free radicals in the hot region and to make them polymerize in the cold regions. Acetylene was shown to be converted into liquid hydrocarbons "almost perfectly."

It seems a shame that further studies were not performed in this area with material systems other than isotopes. In systems in which molecules are large and complex, fast separation rates generally apply. The possibility of controlling reaction equilibrium by CDS, therefore, appears as an exciting possibility in many biological and polymer areas.

CDS Coupled with Adsorption

As far as is known, no one has yet coupled CDS with adsorption. Recent work in the area of parametric pumping, however, suggests that CDS might offer new possibilities here also. Parametric pumping as a separation technique consists of the following essentials as shown in Fig. 15 (Refs. 56 and 57). The liquid to be separated is contained within the column and is alternatively pumped up and down. The alternate heating and cooling of the adsorbent combined with the alternate fluid flow results in a separating action.

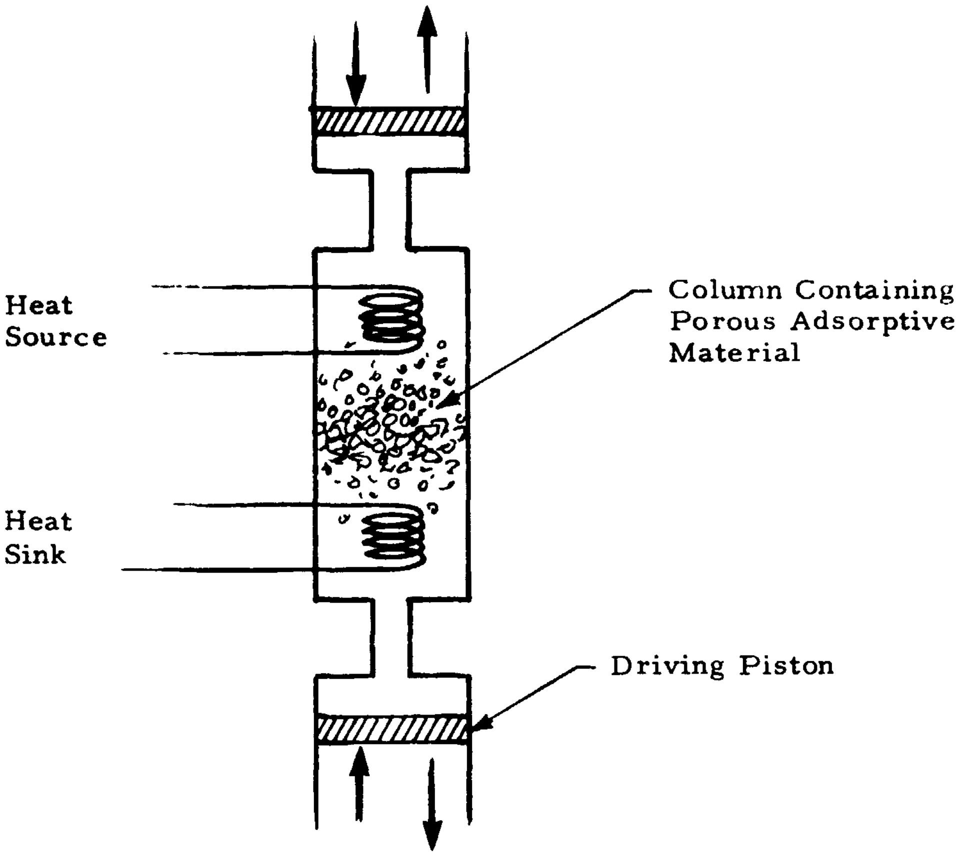


Fig. 15 - Parametric Pumping Essentials

In a CD cell flow reversal could easily be accomplished by reversing the hot and cold walls. The effect of thermal diffusion in such a column, however, is difficult to imagine. Possibly by proper phasing of the flow reversal, thermal diffusion could be made an added separative force. There is still another possibility. A form of natural convection called overstable could perhaps provide the mechanism for alternating flow. In overstable convection flow reversal occurs naturally.

It is conceiveable that a packed CD cell already contains a mechanism for separation. Consider the following CD cell.

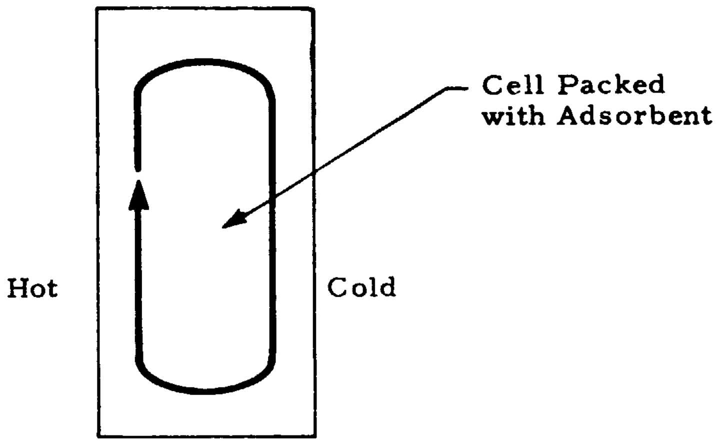


Fig. 16 - Adsorption and CDS

Say the heavier component is also the one most absorbed by adsorbent. Both thermal diffusion and adsorption equilibrium, therefore, would favor driving it to the cold wall and hence to the bottom of the cell.

In the present study a number of experimental studies were conducted on packed columns in connection with the question of CDS efficiency improvement. In one case, as previously mentioned, a 0.721 cm annulus column gave no separation of an aqueous copper sulfate solution without packing, and a rapid, almost complete separation (about 18 hours) when the column was packed with glass wool. Table 1 shows that a 0.721 cm column could separate a aqueous copper sulfate solution to a q_e level of 4.57 in about 22 hours if the gravity level were reduced to 9.88×10^{-5} g_g. Conceivably, the observed separation was the result only of reduced convective flow velocity. The almost complete separation noted, however, is surprising for a q_e value of 4.57 (Appendix E gives experimental details). The possibility presented itself that perhaps adsorption on the glass wool was boosting the separation efficiency. More detailed analyses of various separations in packed columns is indicated.

The startling rapid experimental separation of an aqueous salt in a packed column of relatively large annulus with a relatively small temperature gradient suggests that packed columns may offer the possibility of easy desalination utilizing solar power. Also the possibility presents itself of isotope separations in packed columns utilizing congruently melting compounds such as $LiNO_3 \cdot 3H_2O$. (Possibly a similar uranium compound exists.) Such isotope separations probably would be much less energy consuming than those using molten salts of compounds such as UF_6.

Field Flow and Thermal Field Flow Fractionation (FFF and TFFF)

The concept of using a gravity field and a parabolic flow field to separate macromolecules is dubbed field flow fractionation (FFF). The concept was introduced in 1966 by Giddings (Ref. 58). The essentials of the technique are shown in Fig. 17 below (Ref. 59).

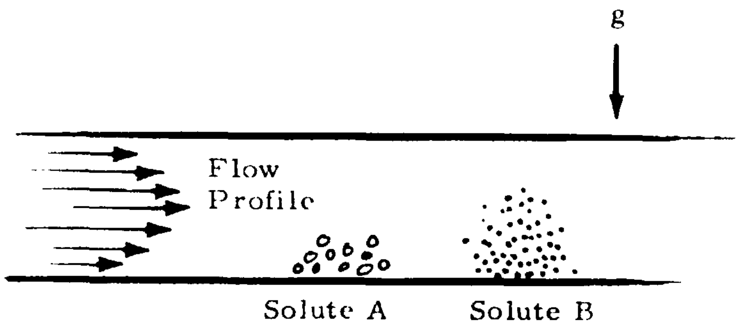


Fig. 17 - Schematic of a Field Flow Fractionation

In Fig. 17 the solutes migrate at different rates in the field flow depending on their penetration into zones of fast flow. It is interesting to note in connection with FFF that a stratification of fine particles can be achieved if a counter-current convective flow is introduced (Refs. 60 and 61), i.e.,

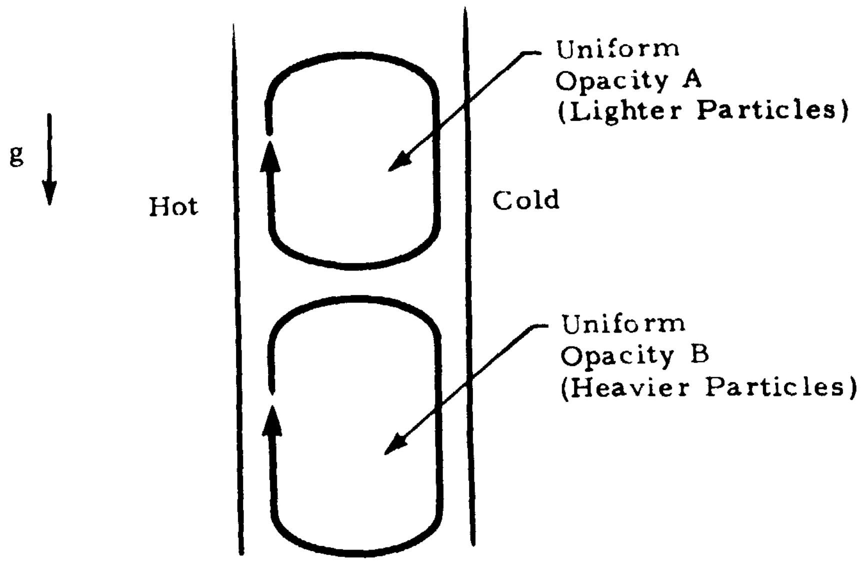


Fig. 18 - Schematic of Stratification Sedimentation

Also of interest in connection with FFF is the phenomenon of "tubular pinch effect" (Refs. 62 and 63). This phenomenon consists of suspensions of spheres forming necklace-like strings of particles in a flow in a tube whose radius is not constant.

The thermal field flow fractionation (TFFF) technique is closely allied to the CD technique. In TFFF (Ref. 64) a temperature difference is superimposed across a parabolic or near-parabolic velocity profile. TFFF is intended for separating macromolecules, having been successfully demonstrated with polystyrene solutes in toluene.

General Comments on CDS Variations and Allied Techniques

None of the mentioned CDS variations and allied techniques have been employed on a commercial scale as far as is known. It is felt that the reasons they have not found commercial applications are either because the technique is too new (thermoelectro CD, parametric pumping, TFF or TFFF) or because the concept was ahead of its time (CD coupled with chemical reactions). The simple basis of the CD technique coupled with the fact that relatively low grade heat is all the energy input that is required to drive the required countercurrent flow indicates that research in this area would yield profitable benefits. It is also expected that the mentioned CD variations will benefit from low-g environments in manners similar to conventional CD.

Section 8

TECHNOLOGICAL APPLICATIONS AND RECOMMENDATIONS FOR FURTHER STUDIES

Space Applications

The following areas of space processing applications appear promising at present:

- Space processing of biologicals by conventional CD or CD coupled with FFF. The main advantage would be larger volumes than could be used on earth.
- Separation of certain specialty isotopes, sulfur 36 from sulfur 32 for example. The larger processing volumes than possible on earth and the "free" solar energy in space would be very advantageous.

CD in space environments may also offer advantages for purification of semiconductor materials. On earth, power hungry techniques like zone melting are commonly used. Before a definite statement can be made, however, a more thorough look into possible problems is required. In this vein, a space CD technique can be imagined whereby a free floating molten sphere would be subjected to a temperature gradient, as shown in the following sketch.

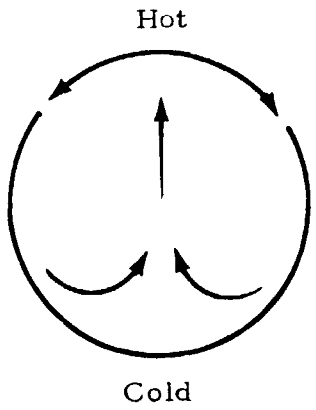


Fig. 19 - Space CD of a Floating Molten Sphere

The imposed temperature gradient would generate the indicated convection currents. The convection currents in this case would be driven not by gravity but by surface tension. In the presence of temperature or concentration gradients, surface tension gradients develop which can drive fluid flow (Refs. 65 through 68). In this case another mechanism in addition to thermal diffusion (and pressure diffusion) for separation would exist – surface adsorption. The efficiency of such a technique, therefore, could perhaps surpass anything that could be done on earth. A number of problems, of course, immediately come to mind, the main ones being how to keep a molten mass positioned without introducing sizable disturbances and how to keep vapor losses at a minimum. Such problems, however, are not seen as insurmountable. Study of thermal separation in floating molten spheres possibly would also generate data that would be of interest to geophysicists. Such a study might help to elucidate how various minerals were originally deposited.

Ground Applications

For some obscure reason, CD has never been adequately explored as a technique for separating aqueous solutions. The reason is hard to understand because the thermal diffusion factors certainly are much larger for aqueous solutions than they are for isotopes. In any case, the rather startling fast separations of copper sulfate in water in a packed column with the relatively low temperature gradient of about 40°C indicates that solar energy and simple packed cells can be used for easy water desalination. A thorough understanding of separation in porous media might be useful also in areas such as pollution studies (i.e., polluted water seeping through the ground), fertilizer distribution, and so on. Also in connection with the overlooked potential of CD with aqueous solutions, isotopes may perhaps be more economically separated by CD if an appropriate hydrated, congruently melting compound can be found. For example, lithium nitrate trihydrate, $LiNO_3 \cdot 3H_2O$, is a compound that melts at 30°C. If subjected to CD, possibly ^6Li could be separated from ^7Li with modest temperature gradients, i.e., $T_H \sim 100^\circ C$, $T_C \sim 30^\circ C$.

The technique should also be considered for uses of the relatively low potential heat that is commonly thrown away and becomes a problem as thermal pollution. Some possibilities include:

- Fractionation or purification of various oils with heat from generating plants or nuclear reaction plants.
- Conducting various polymerization reactions in conjunction with CD with waste heat.

Finally, CD may offer a potential as an energy conversion device. Consider the following situation:

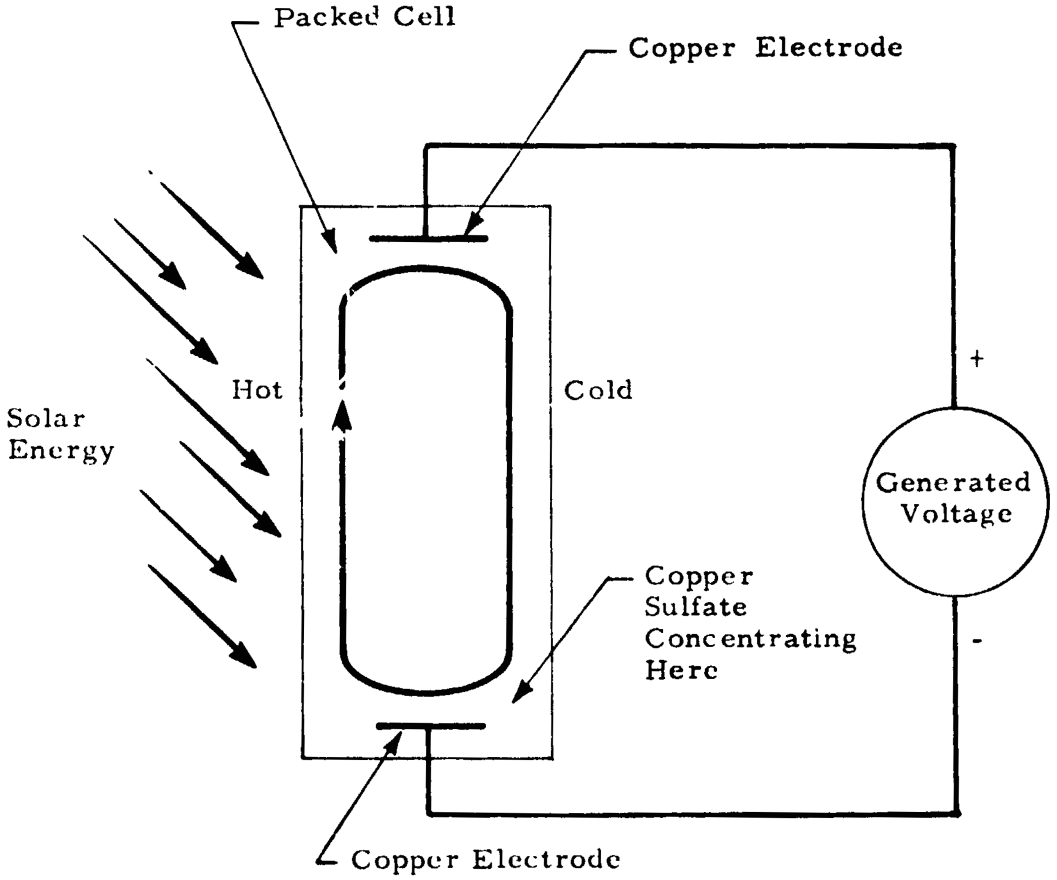


Fig. 20 - An Electrolytic CD Solar Concentration Cell

The CD separation of copper sulfate presents the possibility of a self renewing concentration cell. The question here is how fast can separation work be done. This would determine how much power could be drawn. An interesting aspect of thermal diffusion in this regard is the fairly extensive literature on potentials developed by non-convective "thermocells" (Ref. 69). The subject is beyond the scope of the present study. It is interesting to note, however, that a nonconvective thermocell comprised of lead electrodes and 30% sulfuric acid is reported to have a mean Seebeck coefficient of 2870 $\mu V/^{o}C$. The maximum efficiency is reported as 6.16%, comparable to 10% for the best thermoelectric generators currently used (Ref. 70). An additional sidelight is that a CD apparatus might have potential also as a storage device. A CD cell could concentrate electrolyte on sunny days, the power being drawn on cloudy days. In this area, packed CD cells would certainly be indicated.

Recommended Further Studies

With regard to space applications it will be highly desirable at the first opportunity to experimentally test the theoretical FJO cell parametric relationships in an actual space environment. In such space tests larger wall spacings than are utilized on earth would, of course, be employed. Secondly, while awaiting a flight opportunity, further studies should be conducted aimed at defining a suitable material system for the space experiment. Further studies are also recommended of surface tension convection in free floating spheres and how it may couple with surface adsorption and thermal diffusion to produce separation.

The suggested ground applications indicate more work with aqueous systems and packed columns. Also, to settle the question once and for all, a thorough study of multicellular and turbulent convection on separation efficiency is recommended. Further studies of utilizing waste heat for CD separations are also indicated. Finally, more exploratory and development work with the coupled techniques, i.e., CD plus, field flow fractionation (FFF), electrophoresis, adsorption, and chemical reactions is also indicated.

Section 9

CONCLUSIONS

On the basis of the critical reexamination of the CDS technique, it is concluded that the objectionable features of CDS as is conventionally employed can probably be circumvented by a number of means, among which are: (1) conducting the CD operation in space environments; (2) utilizing modified cell designs; and (3) combining the CD technique with other separation techniques, i.e., electrophoresis, field flow fractionation (FFF), adsorption (parametric pumping), and chemical reactions. Means (2) and (3) would benefit still further from space environments. It is also concluded that the potential of the CD technique for biological and other aqueous solution separations has been largely overlooked. The CD principle appears further to offer novel earth applications such as solar water desalination, energy conversion devices, and a use for waste heat.

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Appendix A

THERMAL DIFFUSION IN ABSENCE OF CONVECTION

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Appendix A

The situation under discussion is typified by a cell such as shown in the following schematic:

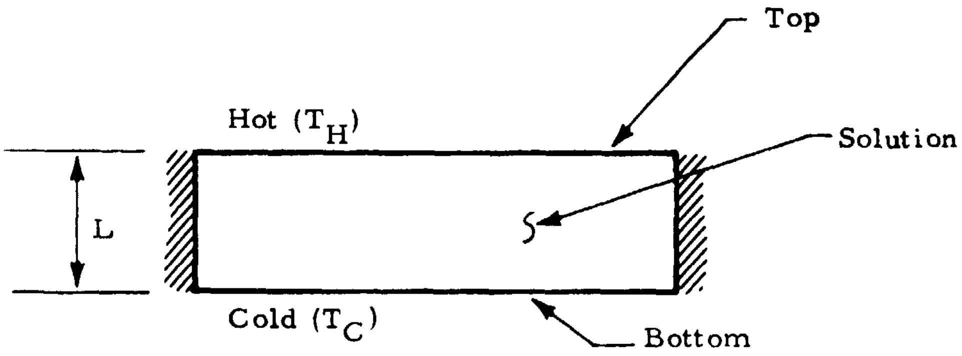

Fig. A-1 - Essentials of a Non-Convective Thermal Diffusion Cell

In the case of a bicomponent gas solution, the equilibrium separation factor for such a cell at steady state is given by the following expression (Ref. A-1, p. 163)

$$q_e = \frac{c_T\,(1 - c_B)}{c_B\,(1 - c_T)} = (T_H/T_C)^{\alpha}$$

where c_T refers to the mole fraction of the lighter component at the top of the cell and c_B the mole fraction at the bottom of the cell. The term α is the thermal diffusion factor (sometimes called the thermal diffusion constant) and is defined by the following relationships:

$$\alpha = k_T/c_1\,c_2$$

$$k_T = D_T/D_{12}$$

where c_1 and c_2 are the mole fractions of the two solution components, D_T is the thermal diffusion coefficient, and D_{12} the ordinary diffusion coefficient. The thermal diffusion ratio, k_T, is strongly concentration-dependent whereas the thermal diffusion factor α is only weakly so. As is readily deduced, the thermal diffusion factor is indicative of the extent of separation achievable by thermal diffusion.

In the case of liquids it has been customary to use the convention of the Soret coefficient instead of the thermal diffusion ratio and factor. The Soret coefficient σ is defined as follows:

$$\sigma = D'/D_{12}$$

where D' is the liquid thermal diffusion coefficient with units of $cm^2/sec^{\circ}C$. The Soret coefficient is formally comparable with α/T. To obtain α from the Soret coefficient one multiplys by the mean temperature, in $^{\circ}K$, of the range in which measurements of the coefficient were made. The relationship between the Soret coefficient and the extent of separation achievable at steady state is given by (Ref. A-3, p. 25).

$$q_e = \frac{c_T\,(1 - c_B)}{c_B\,(1 - c_T)} = e^{\sigma(T_H - T_C)}$$

or

$$q_e = \frac{(c_1/c_2)_T}{(c_1/c_2)_B} = e^{\sigma(T_H - T_C)}$$

If we designate the component of smaller molecular weight as the specified component, a plus value of the Soret coefficient indicates that it will concentrate in the warm region; a negative value indicates concentration in the cold region (Ref. A-2, p. 22).

As indicated by the preceding relationship, the thermal diffusion factor or constant α and the Soret coefficient σ defines the degree of separation at steady state. Values of α range from about 0.01 to 5 and higher and those of the Soret coefficient are typically on the order of $10^{-1} - 10^{-3}/^{\circ}C$.

The relaxation time t_r' for a non-convective cell is (Ref. A-3, p. 31):

$$t_r' = L^2/D_{12}(\pi^2 + A^2)$$

where L represents the distance between the plates and $A = \alpha\Delta T/2\overline{T}$, where $\overline{T}$ is the mean temperature. If the distance between the plates is small, the relaxation time is approximated by (Ref. A-4, p. 111):

$$t_r' = L^2/\pi^2 D_{12}$$

For aqueous solutions t_r' is on the order of 20 days.

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Appendix B

MATHEMATICAL RELATIONSHIPS FOR CELLS WITH CONVECTION

Appendix B

The mathematical treatment of Furry, Jones and Onsager (FJO) (Refs. B-1 and B-2 relating operational equipment parameters for conventional CD cells is generally accepted as adequate for describing qualitatively the functional relationships among the various parameters.

In the following sections a brief outlined of the relationships derived from an elementary version of the FJO theory (Ref. B-1) is presented.

Conventional, Single Stage Vertical Flat Plate and Cylindrical Annulus Cells with No Reservoirs

Cylindrical annulus cells are generally used in practical separations. Although the same general principles apply to both vertical flat plate cells and cylindrical cells, the equations for cylindrical annulus cells are more cumbersome. Present purposes are served adequately by the vertical plate mathematics. The nature of the alternations required for cylindrical annulus cells, however, are indicated.

The essentials of a vertical flat plate cell are shown in the schematic on the following page.

According to the FJO theory, the transport τ_1 of species 1 up the hot wall is defined as

$$\tau_1 = H c_1 c_2 - (K_c + K_d) d c_1/dz \qquad (B.1)$$

where H is a term that represents the flow contributed by thermal diffusion and convection, K_c represents the remixing due to convection currents, and K_d ordinary diffusion back down the cell. At steady state the transport τ_1

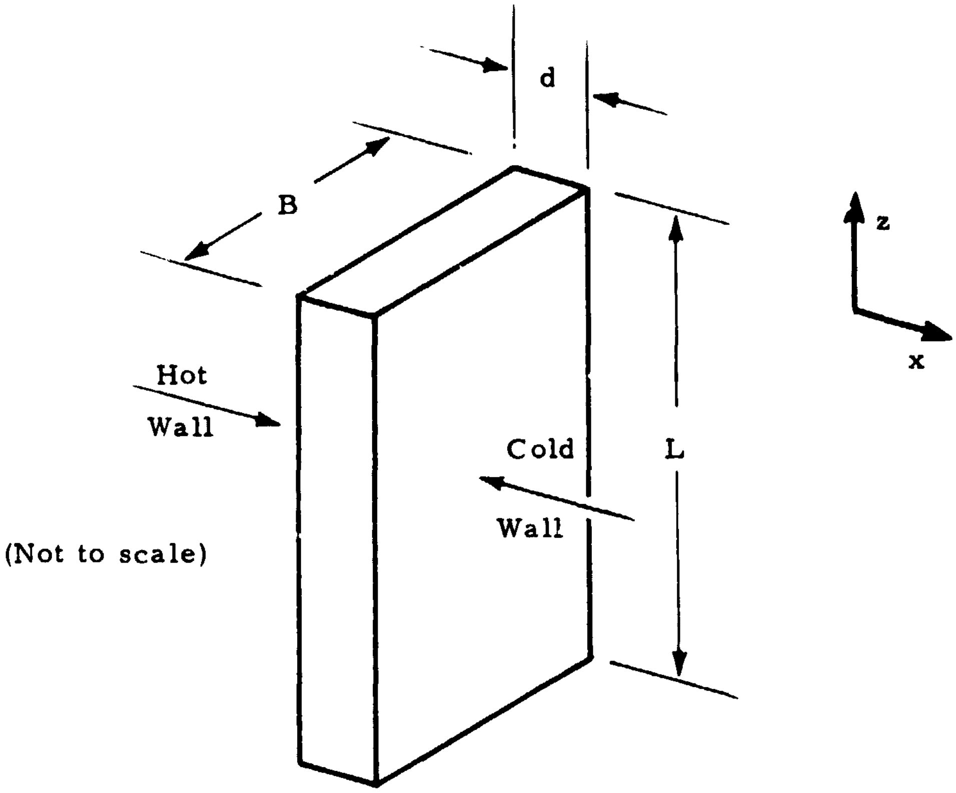


Fig. B-1 – Essentials of Vertical Flat Plate CD Cell

becomes zero and Eq (B.1) then yields the steady state separation factor q_e, i.e.,

$$\boxed{q_e = e^{\frac{H}{(K_c + K_d)} L} = e^{2AL}} \qquad (B.2)$$

where L is the length of the cell. The term $K_s + K_d$ is often replaced by K.

For the vertical flat plate cell, the H and K terms are defined as follows:

$$H = \frac{d^3 \bar{\rho}^2 \alpha \, g \beta B (\Delta T^2)}{6! \, \mu \bar{T}} \qquad (B.3)$$

$$K_c = \frac{d^7 g^2 \bar{\rho}^3 \beta^2 B(\Delta T)^2}{9!\, \mu^2 D_{12}} \tag{B.4}$$

$$K_d = d\bar{\rho}\, D_{12}\, B \tag{B.5}$$

Obviously to maximize q_e, it is necessary to maximize H and mininize K, i.e., or maximize the value of A. The term A can be maximized in a variety of manners depending on which parameter is considered the variable. For example, to maximize A as a function of separaration spacing (d), the following procedure (Ref. B-2)

$$0 = \frac{dA}{dd} = \frac{dH}{Hdd} + \frac{dK}{Kdd}$$

gives an optimum spacing of

$$d_{opt} = \left(\frac{9!}{2}\right)^{1/6} \left(\frac{\mu D_{12}}{\bar{\rho} g \beta \Delta T}\right)^{1/3} \tag{B.6}$$

and an optimum A term of

$$A_{d\,opt} = \frac{(105)^{1/3}}{180}\, \alpha\, \frac{\Delta T}{T} \left(\frac{\bar{\rho} g \beta \Delta T}{\mu D_{12}}\right)^{1/3}$$

If now we follow a similar procedure and optimize A with respect to g we obtain an optimum g term of:

$$g_{opt} = \frac{\sqrt{9!}\, \mu D_{12}}{\bar{\rho}\, d^3 \beta \Delta T} \tag{B.7}$$

where $\bar{\rho}$ is an average density. The corresponding $A_{g\ opt}$ term is:

$$A_{g\ opt} = \frac{\sqrt{70}}{20}\, \frac{\alpha/T}{(1+d)}$$

A sample problem of the change in q_e as a function of g level for a separation of mercury 196 from mercury 200 is shown in Fig. B-2

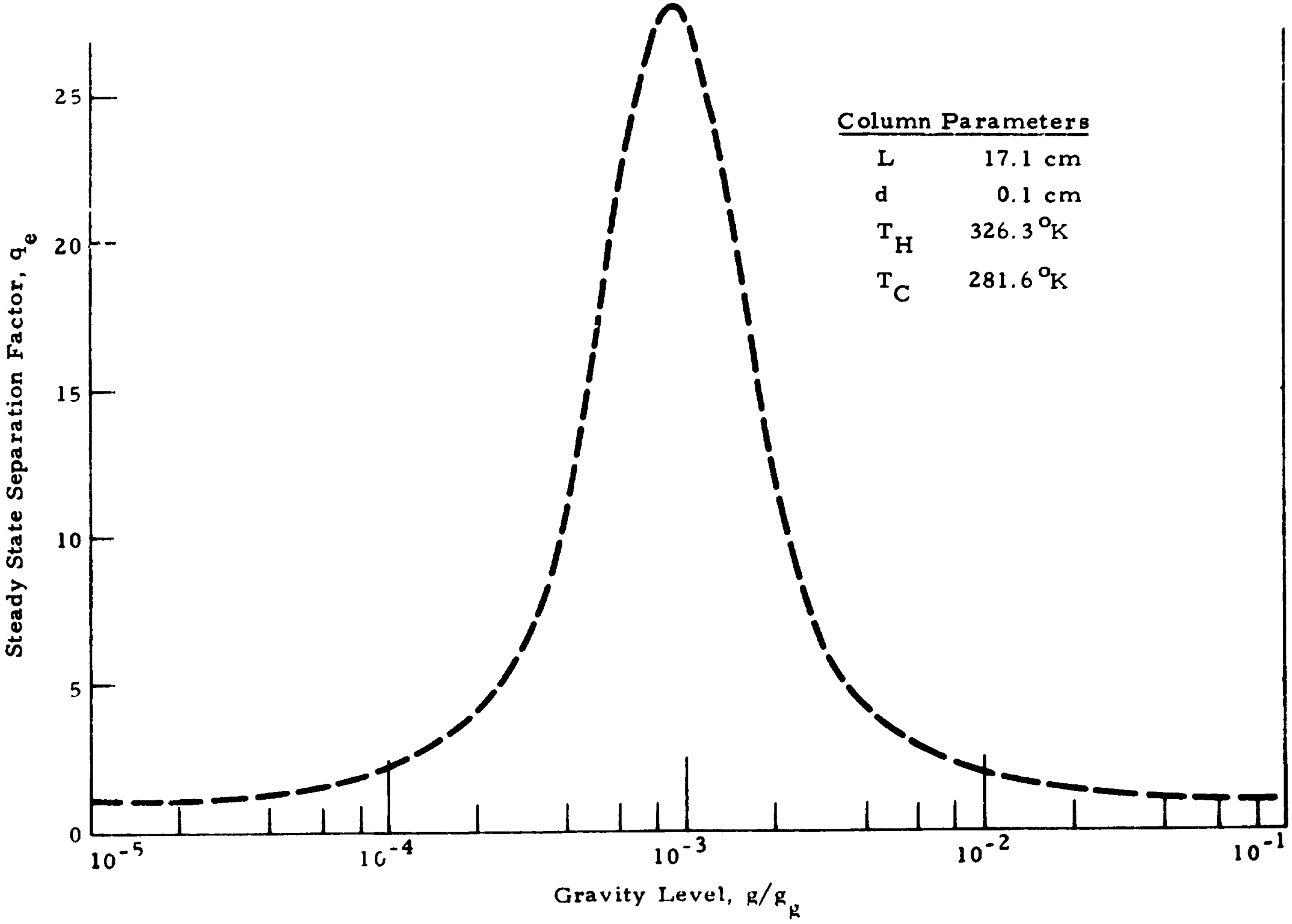


Fig. B-2 – Steady State Separation Factor vs Gravity Level for the Separation of Mercury 196 from Mercury 200.

By further manipulations of the preceding relationships, the following relationship can be derived.

$$\ln q_e = \frac{504 \mu D_{12} \alpha L}{d^4 \overline{\rho} \; \beta \overline{T}} \cdot \frac{g}{g^2 + g_{opt}^2} \qquad (B.8)$$

When working with gases, it is also worthwhile to know the following relationship (Ref. B-2, p. 215)

$$\ln q_e = \frac{a'/P^2}{1 + \frac{b'}{P^4}} \qquad (B.9)$$

where a' and b' are constants for a particular cell and a given set of operating conditions. One problem with trying to increase q_e by pressure increase, however, is added stress on cell walls.

A relaxation time for a vertical flat plate is given by the following equation

$$t'_r = \frac{2X/AH}{1 + \pi^2/(AL)^2} = \frac{2 \rho d B/AH}{1 + \pi^2/(AL)^2} \qquad (B.10)$$

where X is the mass of gas per unit length of column. Equation (B.10) applies only in cases where AL is rather small ($\lesssim 2$). In cases where AL is larger, a more complicated equation applies (Ref. B-2, p. 179).

The rate at which equlibrium is approached is not linear with time. In the case where AL (and $c_1 << 1$) is small compared with unity, the following expression gives the transient separation factor (Ref. B-2, p. 179):

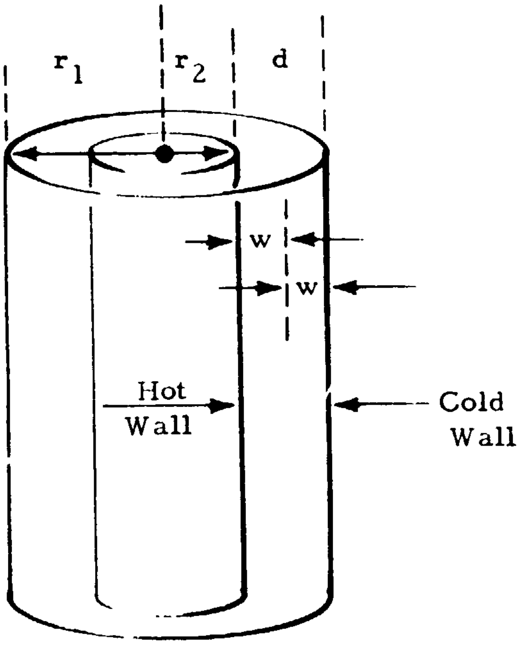
$$q \sim \frac{c_e}{c_s} = 1 + 4H \left(\frac{t}{\pi X K} \right)^{1/2} + \ldots \qquad (B.11)$$

This equation indicates a rapid increase at the beginning of a separation followed by a slower increase; also the equation indicates that the initial rise in concentration is independent of the length of the column.

In the case of cylindrical annulus cells, i.e., see schematic on following page, the same general considerations apply. The H and K terms, however, are corrected for cell shape by means of simple, but rather cumbersome, functions. The reader is referred to Ref. B-2 for details. It may be mentioned, however, that as r_1/r_2 decreases the mathematics approach those for the vertical plate case.

It is interesting to note that B, the cell width, usually cancels out of the steady state relationships. In transient cases, i.e., equation (B.11), however, B remains a factor. In cases of continuous flow (Appendix C) also, B is a factor that cannot be ignored.

(Not to scale)

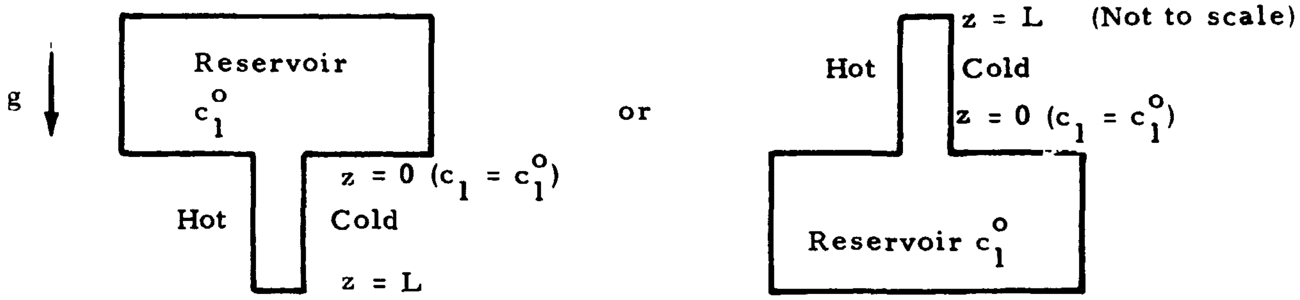


d = 2w

Fig. B-3 – Cylindrical Annulus Cell

Single Stage Cells with an Infinite Reservoir at One End

In the case of a simple closed vertical plate (cylindrical annulus) cell in which a reservoir is connected to one end, i.e.,



For mixtures in which the heavier component is to be separated.

For mixtures in which the lighter component is to be separated.

Fig. B-4 — Essentials of Cells with Reservoir at One End

c_1 at $z = 0$ remains constant at c_1^o. Given a separation factor, therefore, the absolute final concentration at the enriching end can be easily calculated. For this case the equations for steady state separation factor are the same as for the preceding cases.

The equations for time to reach a given level of separation and for relaxation time to steady state, however, are:

$$q - 1 = (q_e - 1)(1 - e^{-t/t'_r}) \qquad \text{(E.12)}$$

where t is the relaxation time and can be approximated by the following relationship

$$t'_r \approx \frac{\rho d B L}{H} \left\{ \frac{q_e - 1}{2AL} - 1 \right\} \qquad \text{(B.13)}$$

In these equations it is assumed that the reservoirs are of infinite capacity and c is everywhere very small and AL is not (Ref. B-2).

Condition for Avoidance of Turbulence

Onsager and Watson (Refs. B-3) derived the approximation

$$Re \cong 2\left(\frac{K_c}{K_d}\right)^{1/2} \tag{B.14}$$

where Re is the Reynolds number. They also showed experimentally that turbulence occurs when Re exceeds about 25. The following set of operations shows that

$$Re \cong 2\left(\frac{K_c}{K_d}\right)^{1/2} = 2\,\frac{g}{g_{opt}} \tag{B.15}$$

$$2\left(\frac{K_c}{K_d}\right)^{1/2} = 2\left(\frac{d^6 g^2 \bar{\rho}^2 \beta^2 (\Delta T)^2}{9!\,\mu^2 D_{12}^2}\right)^{1/2}$$

$$= 2\,\frac{d^3 g \bar{\rho} \beta\, \Delta T}{9!\,\mu D_{12}} = 2\,\frac{g}{g_{opt}}$$

Setting the condition that Re should be less than 25, we obtain

$$Re < 25 > 2\,\frac{g}{g_{opt}}$$

or

$$\frac{g}{g_{opt}} < 12.5 \tag{B.16}$$

Re is usually set at 10 to be on the safe side. The present study, however, for reasons of calculational convenience will use as a criterion of turbulence

$$Re < 20 \qquad \text{so that} \qquad \frac{g}{g_{opt}} < 10$$

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Appendix C

EFFECT OF CONTINUOUS FLOW ON SEPARATION EFFICIENCY

Appendix C

It is sufficient for present purposes to assume that feed at some desired constant concentration, c_i, and flow rate, σ, in grams per second, can be supplied to the separation column. Taking as an example the case of sulfur isotope separation in the molten state, Case E3 in Table 1, the following formula can be used to indicate the effect of flow rates on separation. If the flow through the column is so slow that the full steady state separation is achieved, a q_e of 1.56 would result in a final concentration c_f of 2.12×10^{-4}, i.e.,

$$q_e = 1.56 = \frac{c_f(1-c_i)}{c_i(1-c_f)} = \frac{c_f(1 - 1.36 \times 10^{-4})}{1.36 \times 10^{-4}(1-c_f)}$$

$$c_f = 2.12 \times 10^{-4}$$

and

$$\frac{c_i}{c_f} = 0.641$$

For the case where the desired component concentration is much less than one, the following formula applies

$$\frac{c_i}{c_f} = \frac{e^{-2AL(1+\frac{\sigma}{H})} + \frac{\sigma}{H}}{1 + \frac{\sigma}{H}}$$

The definitions of the terms A and H are in Appendix B. Formulas for various other concentration ranges are given in Ref. 1. Utilizing the preceding formula and setting σ at 1 gm per day, and the width of the cell at

10 cm the following ratio would be obtained

$$\frac{c_i}{c_f} = 0.648$$

corresponding to a c_f of 2.01×10^{-4}. Other formulas for different concentration levels are given in Ref. C-1.

REFERENCE

C-1. Jones, R.C., and W.H. Furry, "The Separation of Isotopes by Thermal Diffusion," Rev. Mod. Phys., Vol. 18, 1946, pp. 186-137.

Appendix D
BIBLIOGRAPHY OF REFERENCED SEPARATIONS

Appendix D

LIQUID PHASE SEPARATIONS

An extensive bibliography is given in Ref. D-1 of Soret coefficients for various aqueous and organic solutions. Additional Soret coefficients and thermal diffusion factors for other varied, solutions are given in the following indicated references.

Polymer solutions (D-2)
Non-aqueous electrolytic solutions (D-3)
Isotopes in liquid metallic solution (D-4, D-5, D-6)
Various metallic solutes in liquid metals (D-7, D-8, D-9)
Isotopes in molten salts (D-10)

A multitude of separations by the CD technique therefore are possible. Specific separations conducted in the liquid phase by the CD technique are given in the following list. The list is not exhaustive. Enough examples were chosen, however, to give a good indication of the types of separations that are feasible by the CD technique.

- Biological Solutions and Suspensions

Viruses and ribosomes (D-11)
Deoxyyribonucleic acid (D-11)
Carbohydrate solutions (D-12, D-13)
Homologous fatty acids (D-14)
Monomer and dimer unsaturated fatty acids (D-14)
Dibasic acid esters (D-14)
Primary and secondary amines (D-14)
Aromatic heterocyclic amines (D-14)
Polysaccharides (D-14)
Mono-, di-, and tri-esters of polyols (D-14)
Polyoxyethylene sorbital esters of resin and fatty acids (D-14)
Fatty acids and polyol esters (D-14)
Mono- and di-carboxylic acids (D-14)
Alicyclic and aliphatic alcohols (D-14)

Alkyl amines and hydrocarbons and phenols and aromatic hydrocarbons (D-14)
Methyl esters of soybean oils, mixed soybean oil esters resulting from partial methanolysis, and crude mono-, di-, tri-oleate mixtures were fractionated (D-14)
Papain — diastase solution (D-13)
Ergosterol and cholesterol in chloroform solution (D-13)
Casein, gelatin, egg albumin, papain, and diastase of malt solutions (D-13)

- Aqueous Electrolyte Solutions

$Cu SO_4$ (D-15)
Cu Br (D-15)
$Co Cl_2$ (D-15)
$Zn SO_4$ (D-16)

- Aqueous Non-Electrolytic Solutions

Water and 1-propanol. These compounds from an azeotropic boiling mixture (D-17)
Water from ethyl alcohol (D-18, D-19, D-1)

- Polymer Solutions

Polystyrene in toluene (D-20)
Polymethyl methacrylate in various solvents. The separation was so rapid in this case that a CD column was not necessary (D-21)

- Organic Isomers

Cis and trans isomers of 1, 2 dimethyl-cyclohexane were separated. These isomers have identical molecular weights. The cis isomer concentrated at the bottom of the column and the trans isomer at the top (D-18)
Ortho xylene and
  meta xylene (D-18)
  para xylene (D-18)
  n-heptane and triptane (D-18)
  Iso-octane and n-octane (D-18)
  2 — methylnaphthalene and
  1 — methylnaphthalene (D-18)
  n-pentane and neo-pentane (D-22)

- Binary Organic Mixtures

<u>Separations achieved with:</u>

2, 4 — dimethylpentane and cyclohexane. These compounds have almost identical boiling points, i.e., 80.50 and 80.74°C (D-18)

An azeotropric mixture of benzyl alcohol and ethylene glycol (D-18)

Cyclohexane and

- benzene (D-18)
- toluene (D-18)

Cetane (n-hexadecane) and

- cumene (isopropylbenzene (D-18)
- methylnaphthalene (D-18)
- benzene (D-18)
- toluene (D-18)
- m-xylene (D-18)
- mesitylene (D-18)
- carbon tetrachloride (D-18)
- n-heptane (D-18)
- decalin (decahydronaphthalene) (D-17)

Benezene and

- octadecane (D-18)
- hexadecane (D-18)
- carbon tetrachloride (D-18)
- cyclohexane (D-18)
- n-heptane (D-18, D-23, D-19)
- bibenzyl (D-24)
- biphenyl (D-24)
- trans-stilbene (D-24)
- o-terphenyl (D-24)
- diphenylmercury (D-24)

Cumene and methylnaphthalene (D-18)

Methylcyclohexane and

- n-heptane (D-18)
- isooctane (D-18)

n-octane and n-decane (D-18)

Toluene and

- chlorobenzene (D-18)
- methylcyclohexane (D-17)

n-octane and 2, 2, 4 trimethylpentane (D-17) n-heptane and 2, 2-dimethylpentane (D-17)

Cyclohexane and 2, 2, 3-trimethylbutane (D-17)

2, 2-dimethylpentane and

  2, 2-dimethylbutane (D-17)
  3, 3-dimethylpentane (D-17)

2, 2 3-trimethylbutane and

  ethanol (D-17)

Ethylbenzene and 2-ethoxyethanol. These compounds form an azeotropic boiling mixture (D-17)

Chlorinated aromatic hydrocarbons (D-14)

<u>Separations not achieved with</u>:

Meta- and para-xylene (D-18)

Benzene and cyclohexane (D-17, D-18)

Toluene and methylcyclohexane (D-18)

Cetane and cyclohexane (D-18). Separation was achieved however in another study (D-17).

Aliphatic alcohols and fatty acids (D-39)

- Ternary Organic Mixtures

n-octane, methylcylohexane, and cumeme (D-18)

Ortho-, meta-, and para-xylene (D-18)

- Oil Fractionations

White oil (D-17)

Solvent refined, mid-continent lube oil (D-17)

Paraffinic type oils (D-17)

Naphthenic type oils (D-17)

Mid-continent paraffin distillate (D-25)

Furfural extract (D-25)

Furfural extracted raffinate (D-25)

Tall oil (D-26)

Bromotrifluoroethylene telomer fluid (D-27)

C, 2

Aromatic coal tar hydrocarbons (D-14)
Naphthenic waxes and oils (D-28)

- Isotopic Solutions

Heavy water from ordinary water (D-29)
Benzene
$C_6H_6 - C_6D_6$ (D-30)
$^{13}C\,^{12}C_5 - ^{12}C_6H_6$ (D-30)
Cyclohexane
$C_6D_{12} - C_6H_{12}$ (D-30)
$^{13}C\,^{12}C_5H_{12} - ^{12}C_6H_{12}$ (D-30)
Carbon disulfide
$C^{32}S_2 - C^{32}S^{34}$ (D-30)
1-Chloropropane
$C_3H_7\,^{35}Cl - C_3H_7\,^{37}Cl$ (D-30)
Bromoethane
$C_2H_5\,^{79}Br - C_2H_5\,^{81}Br$ (D-30)
$^{235}UF_6 - ^{238}UF_6$ (D-31)

GAS PHASE SEPARATIONS

Values of α for some fifty gas pairs are given in Ref. D-32. Information on actual CD separations and α values are given in the following references.

Br_2 and Cl_2 in noble gases (D-33)
$^{13}C\,^{16}O - ^{12}C\,^{16}O$ (D-34, D-35)
Argon-neon (D-33)
Krypton-argon (D-33)
$H_2 - D_2$ (D-36)

T_2 - H_2 (D-35)

^{3}He - ^{4}He (D-35)

$^{12}CO_2$ - $^{14}CO_2$ (D-35)

$^{12}CH_4$ - $^{13}CH_4$ (D-35)

$^{16,16}O_2$ - $^{16,18}O_2$ (D-35)

^{20}Ne - ^{21}Ne (D-35)

$H\,^{35}Cl$ - $H\,^{37}Cl$ (D-35)

Ortho- and para-hydrogen (D-37)

Gas pairs (D-38)

- CO_2 - C_3H_8
- CO_2 - N_2O
- N_2O - C_3H_8
- CO - C_2H_4
- CO - N_2
- N_2 - C_2H_4

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Appendix E
SUMMARY OF EXPERIMENTAL STUDIES

Appendix E

Separations in four different types of CD cells were studied in the course of the present study. These consisted of conventional CD columns, packed CD columns, rotated CD columns, and flat plate cells. The objective of the experimental studies was threefold:

- To obtain a knowledge of the practical problems involved with each type of cell.
- To determine the effect of small pressure gradients on separation.
- To generate convective multicells and spiraling flow and to determine the effect of these flow patterns on CDS efficiencies.

The work accomplished in each area is summarized by type of cell.

Conventional CD Columns

The experimental work with conventional CD columns was performed by Barbara Facemire of the NASA-George C. Marshall Space Flight Center. The apparatus used in this phase of the study was the commercial Thermo-Search II apparatus (made by Technical Research Instruments, Inc., 288-B Murray Drive, King of Prussia, Pennsylvania, 19406, telephone 215-265-0832). The essentials of the apparatus are shown in Fig. E-1. Essentials of the columns provided with the Thermo-Search II are shown in Fig. E-2. The Thermo-Search II can monitor and control the hot and cold flows from the water baths from under 0.2 L/min to over 2 L/min. (Further details in Ref. E-1).

The spacings between hot and cold walls that were utilized were 0.1, 0.2, 0.3, and 0.4 mm. The lengths of the cells were all 30.5 cm. The temperature of the hot and cold flows were either $56 \pm 3^{\circ}C$ and $22 \pm 2^{\circ}C$ or $50 \pm 2^{\circ}C$ and $5 \pm 2^{\circ}C$. Separation of a series of copper culfate solutions of 1.0 M concentration were studied as a function of wall spacing. The concentrations of the

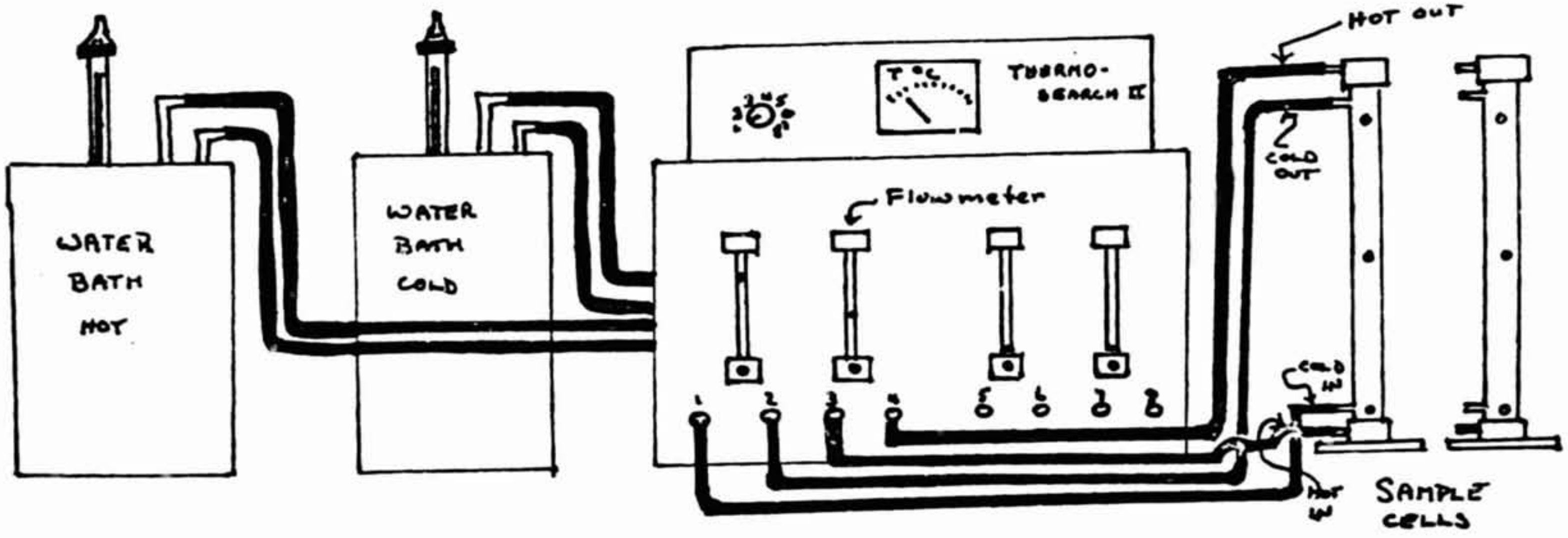


Fig. E-1 - Schematic of Soret Separation Apparatus

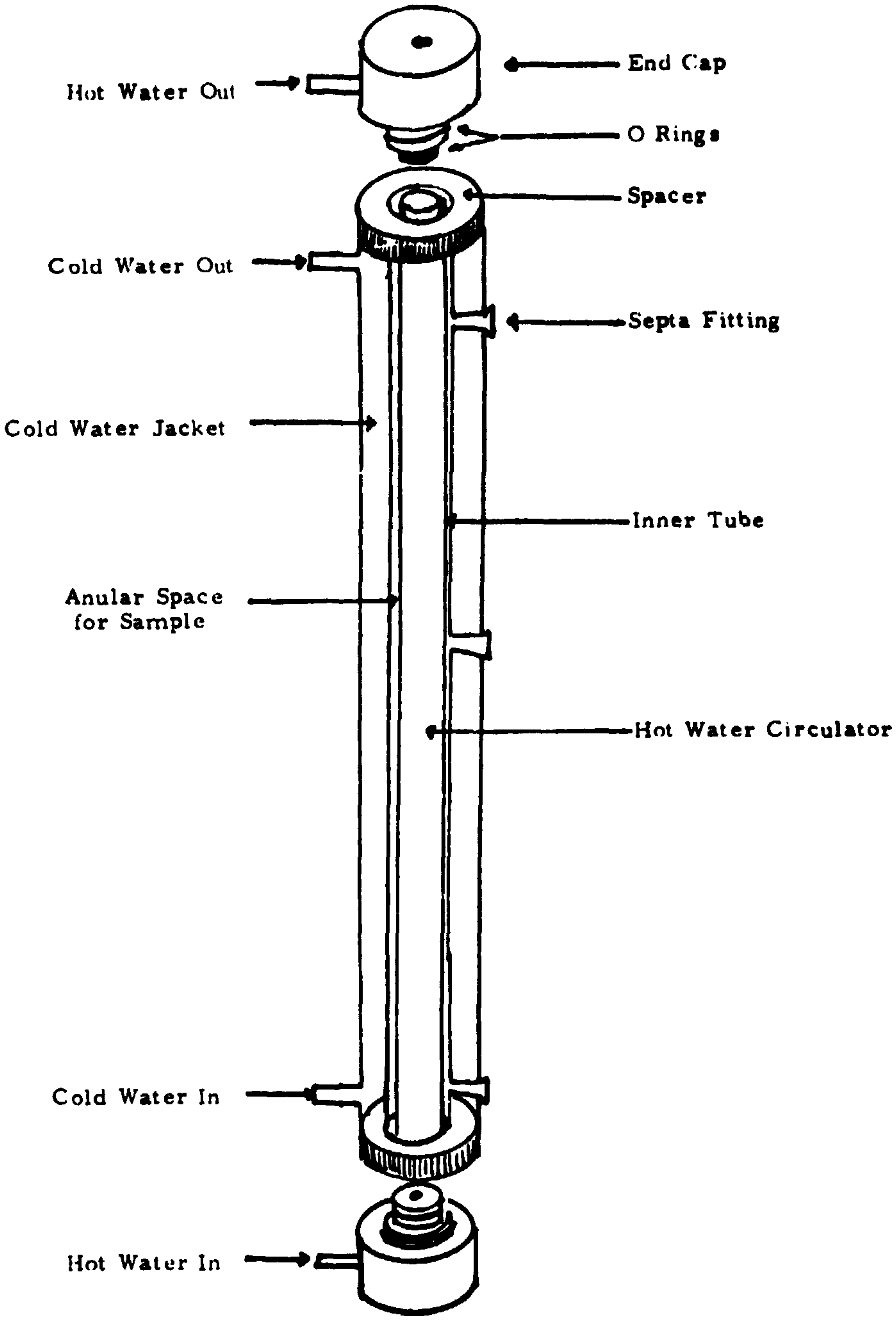


Fig. E-2 - Details of Sample Cell

solutions were determined by means of an ABBE-3L Refractometer. Table E-1 shows some typical data on the effect of cell spacing on separation level achieved. Table E-2 shows some typical data on separation as a function of time.

The interesting result of the experiments is that the 0.1 mm wall spacing (see Table E-1) gave the worst separation and the 0.4 mm wall spacing generally the best separation, contrary to theory. (Variations in the sizes of the samples taken for analysis caused some minor variations.) The most probable explanation is that at the smaller wall spacings misalignment and wall imperfections caused a stagnation of the solution in some regions. The result emphasizes the critical nature of the wall spacing. An attempt to identify the convective flows at each wall spacing by injecting dye (red food coloring) interestingly enough indicated no countercurrent convection at any of the wall spacings. The solutions containing the dye showed the behavior shown in Fig. E-3. This result is indeed puzzling.

Packed Columns

In this phase, CD columns were constructed from ordinary laboratory glass tubing and packed with a variety of materials. No extraordinary measures were taken to align the columns; i.e., the columns were judged to be reasonably well aligned if they looked straight. Table E-3 shows some selected results of these runs.

As discussed in Section 7, the data givenin Table E-3 is rather difficult to accept solely on the basis of reduced convection. It would appear that adsorption aided separation in the packed columns.

Rotated Columns

This portion of the study was performed at the University of Texas, Austin, under the direction of Dr. E. L. Koschmieder. Mr. William Jackson, a graduate student, performed the laboratory separations. As mentioned

Table E-1

EFFECT OF WALL SPACING ON SEPARATION OF A 1.0 M AQUEOUS COPPER SULFATE SOLUTION

Gap Width (mm)	Time (hours)	Molarity			Sample Size Analyzed (ml)
		Top	Middle	Bottom	
Proportional Analysis Samples					
0.1	5	0.850	0.920	1.14	0.03
0.2	5	0.760	0.940	1.280	0.06
0.3	5	0.900	0.920	1.340	0.09
0.1	24	0.740	0.800	0.920	0.03
0.2	24	0.700	0.750	2.460	0.06
0.3	24	0.660	0.760	2.080	0.09
0.4	24	0.520	0.750	2.320	0.13
Equal Analysis Samples					
0.1	5	0.920	0.920	1.100	0.06
0.2	5	0.760	0.940	1.280	0.06
0.3	5	0.860	0.900	1.340	0.06
0.4	5	0.700	0.900	1.520	0.06
0.1	24	0.760	0.840	0.920	0.06
0.2	24	0.700	0.750	2.460	0.06
0.3	24	0.680	0.760	2.260	0.06
0.4	24	0.520	0.700	2.700	0.06

Table E-2
SUMMARY OF TIME-DEPENDENCE TESTS

Time of Run (hours)	Separation Efficiency C/C_o		
	Top	Middle	Bottom
0.5	1.0	1.0	1.0
1.0	0.935	1.0	1.022
2.0	1.0	1.0	1.087
3.0	0.95	0.92	1.12
5.0	0.85	0.86	1.02
8.0	0.82	0.84	1.06
20.0	0.76	0.85	1.48
25.0	0.72	0.80	2.08
50.0	0.72	0.84	2.35

Note: 2 mm wall spacing.

Table E-3
EXPERIMENTAL SUMMARY OF PACKED COLUMN SEPARATIONS

Run	Initial $CuSO_4$ Conc.	Cell	d (cm)	T_H (°C)	T_C (°C)	ΔT (°C)	Packing	Sep. Noted in †	Approximate q*
E	0.127 M	A	0.182	48.8	14.3	34.5	Glass Wool	72 hrs	25
F	0.127 M	A	0.182	48.8	14.3	34.5	None	no sep.	1
H	0.127 M	A	0.182	51	11	40.0	Glass Wool packed denser than Run E	2 hrs	8
M	0.134 M	C	0.721	52	12	40.0	Glass Wool	18 hrs	∞
O	0.134 M	E	0.329	52	12	40.0	Dylite ‡	96 hrs	9
P	0.123 M	C	0.721	52	12	40.0	Glass Beads	no sep.	1

† The time is the time separation was noted. This actual time for the observed level of separation noted may have been somewhat shorter.

‡ Dylite F-40 – expandable polystyrene.

* $(\text{Conc. in mole/L})_{\text{bottom of column}} / (\text{Conc. in moles/L})_{\text{top of column}}$

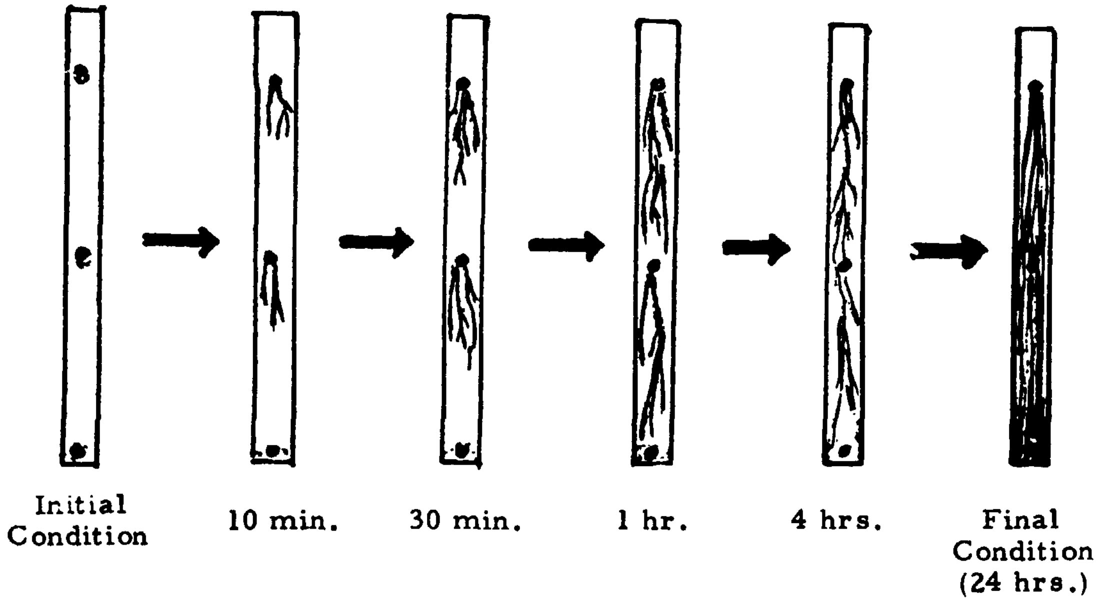


Fig. E-3 - Progression of Dye in Flow Tests previously, the objectives of this portion of the work were to determine the effect of small pressure gradients and of spiraling or multicellular convection on separation efficiencies.

Description of Apparatus

A schematic cross section of the apparatus used is shown in Fig. E-4. The apparatus consisted of two concentric brass cylinders marked (1) and (2) on Fig. E-4. The gap between these cylinders was filled with the experimental fluid. The cylinder walls were heated or cooled, respectively, by water circulated along the cylinder walls. The brass cylinders (1) and (2) were 25.4 cm long; the inner diameter of the outer cylinder was 7.62 cm; and the outer diameter of the inner cylinder was 5.715 cm. The radii of both cylinders were specified to be accurate to at least 0.00254 cm. The outer cylinder was 0.3175 cm and the inner cylinder 0 238 cm thick. The gap width between both cylinders would be varied by slipping cylinders with different outer diameters over the inner cylinder. Such a cylinder is indicated in Fig. E-4 by the mark (7). The following gap widths were used: 0.953 cm for the regular gap between both brass cylinders and 0.254 cm, 0.127 cm, and 0.0508 cm for three gaps between the outer cylinder and different inner cylinders. Note the importance, in particular, for the smallest gap the accuracy of the radii of the cylinders. The fluid in the gap between both cylinders was contained at the bottom by a lucite ring marked (3), which ring was sealed with Dow Corning silastic. The fluid was covered on top by a lucite lid (5), which is sealed toward the side by an O ring. Probes of the fluid were taken with syringes through a hole in the lid and the bottom. The fluid column between the bottom ring and the lid was 20.32 cm long.

The temperatures of the brass cylinders were set as follows. Water was circulated upward through a 1.27 cm wide center hole in the lucite piece (4) which filled nearly the entire inner cylinder. At the upper end of the lucite piece the flow hit a conical bakelite piece (6) and was forced to spread sideward. The flow then moves along the wall of the inner brass cylinder in a 0.159 cm wide gap between the lucite and the cylinder. This arrangement

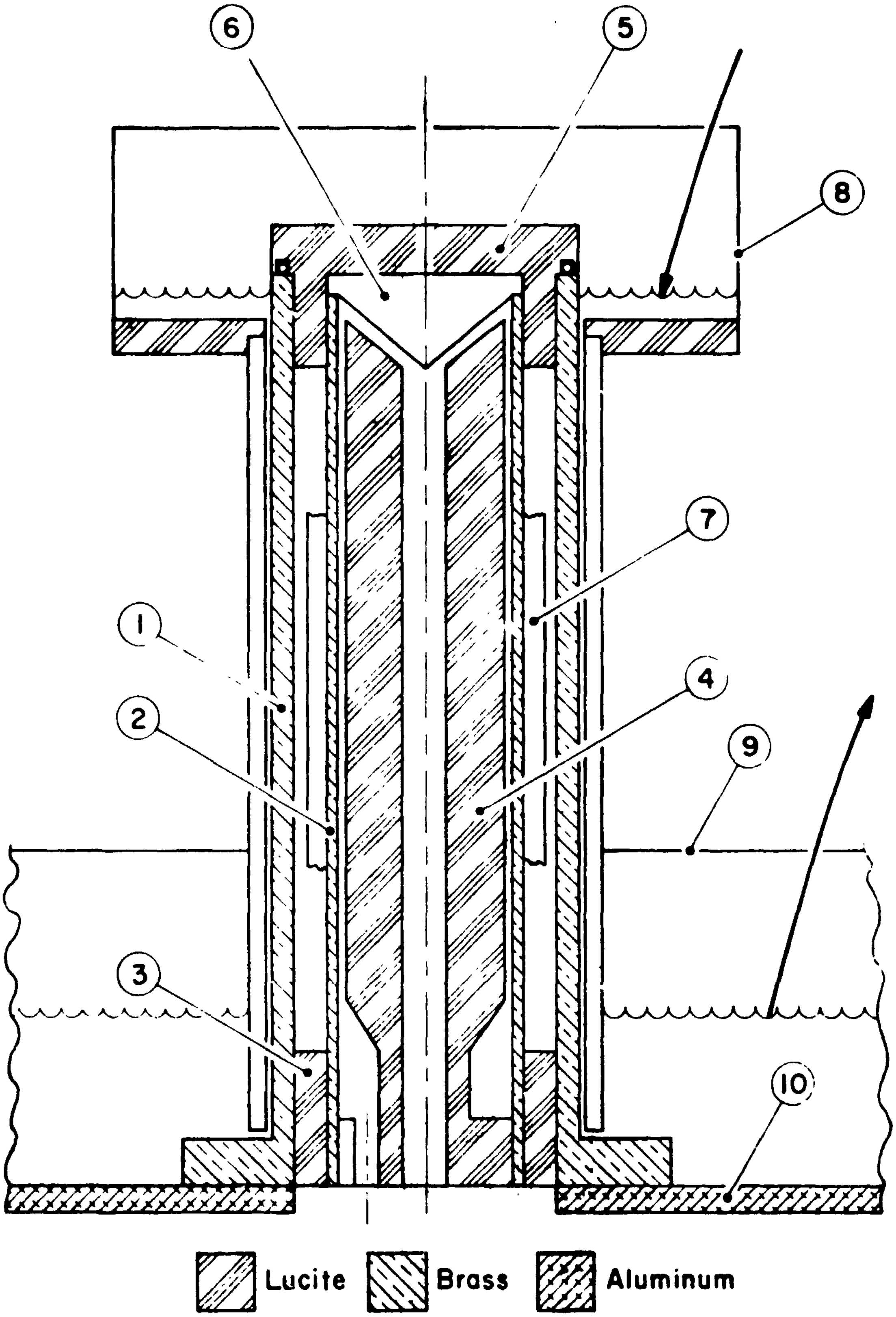


Fig. E-4 - Cross Section of Separation Apparatus guaranteed a uniform temperature distribution along the wall of the inner cylinder. The cooling or heating water was discharged from the inner cylinder through three equidistant holes at the lower end of the lucite piece. The temperature of the outer cylinder was set in a corresponding way. Water was fed through a hose into an open circular container (8) around the top of the apparatus. From there the water flowed through a narrow gap between the outer brass cylinder and a surrounding lucite cylinder. The rate of flow was controlled through a narrowing at the lower end of the lucite cylinder, ensuring that the entire brass cylinder was wetted and a uniform temperature along its wall was obtained. After passing the cylinder the water was collected in a circular container (9) from which it was removed by a suction pump. Flow rates along the inner and outer cylinder varied between 50 to 100 cm/sec. The water was forced into the inner cylinder from below through a rotary gland. The heating or cooling water was supplied by two 10-gallon Aminco constant temperature baths, which controlled the water temperature to $\pm 0.1^{o}C$. The temperature difference between both cylinders was, in most of the experiments, $20^{o}C$. The mean temperatures of the test fluid in the gap between both brass cylinders was equal to room temperature.

It was possible to heat either the inner or the outer cylinder electrically, as was done in several previous separation experiments, but it seemed desirable to be able to reverse the direction of the radial temperature gradient between both cylinders. Since cooling could be accomplished only by circulating a fluid along the wall to be cooled, the arrangement as described above had to be used in the present experiments.

The apparatus was mounted on a circular bakelite plate 1.27 in. thick. This plate, in turn, was mounted on a circular aluminum plate (the base of the turntable). The turntable, which had been used before, was improved for these experiments by an additional heavy thrust bearing which reduced a slight wobble that had occurred previously. Also, for these experiments, the drive of the turntable was improved by a new 1/4 hp Graham variable speed drive. As it turned out, the rotation rate did nevertheless decrease by about 12% when the motor was run continuously over a couple of days. The rotation rate was measured electronically with a microsecond counter. The axis of the apparatus was aligned with the vertical and the axis of the apparatus was made to coincide with the axis of the turntable.

Slow Rotation Experiments and Results

The experiments were made as follows: the temperatures of the cylinder walls were set first by circulating water of different temperature along them. The gap between the cylinders was then filled with the test fluid, an ethanol-water solution of 50% weight concentration. When the solution was in the gap a probe of about 0.4 ml was taken in order to determine the exact concentration by measuring the refractive index of the solution. The refractive index was measured with an ABBE-3L refractometer manufactured by Bausch and Lomb.

As soon as the solution was poured into the annulus, rotation was started, and the time of revolution was measured. The dial setting for the motor was maintained throughout each experiment, although the time for one revolution increased up to 2%, though this increase took place very slowly over a couple days. Samples of the test fluid were originally taken at timed intervals. However, it was learned that this procedure disturbed the concentrations later on. In most of the experiments the concentration was measured again only at the end of the experiment, in most cases after three days of continuous operation. Separation was then determined by subtracting the ethanol concentration at the bottom from that at the top.

The first experiments were made with the 0.953 cm gap. It was, of course, realized that this gap was substantially wider than the gaps used normally in separation experiments which are of order of 1 mm. However, it was hoped that rotation would have a substantial effect on separation and therefore this gap width was tried first. Finally it was assumed that the centrifugal circulation in a very narrow gap might be suppressed by boundary layer effects, and that therefore a large gap might be advantageous.

However, the change in concentration measured with the 0.953 cm gap was within the error with which the refractive index can be measured and hence insignificant. Experiments were then made with gaps of 0.254, 0.127 and finally 0.0508 cm. At 0.02 inches, the experimental errors associated with the separation were tolerable.

At 0.0508 cm, which made it indeed a narrow gap, the accuracy of the machining of the cylinder walls became important, but the separation (concentration at the top of the column minus the concentration at the bottom of the column) was then in the 0.15 to 0.20 range after three days of operation. The measurements were first made with a nagative temperature gradient in the gap, that means with a warm inner and a cold outer cylinder. As Fig. E-5 shows, these measurements indicate a slight increase of separation with Ω. This increase may still be, within the error margin, compatible with a constant separation. In order to check on this result the temperature gradient across the gap was reversed, that means that the outer cylinder was now made warm. In this case the measurements indicate (see Fig. E-5) that there is a small decrease of separation with Ω. Since the centrifugal circulation reverses with a reversal of the temperature gradient, the decrease of separation in the case of a positive temperature gradient seems to confirm the increase of separation with a negative temperature gradient. It thus seems as if the small centrifugal force equivalent to about 2×10^{-3} g has, indeed, an effect on the separation in a rotating laterally heated annulus.

Flat Plate Cells (Unpacked and Packed)

The objective of this phase of the experimental work was primarily to demonstrate the effect of multicellular convection on separation. The experimental cells used in this study consisted of two rectangular boxes measuring 35.6 x 10.2 x 2.54 cm and 35.6 x 10.2 x 1 cm constructed with 1.91 cm thick plexiglass plastic material and 0.317 cm thick aluminum (2.54 cm cell) or stainless steel (1 cm cell) plate for the top and bottom surfaces to ensure isothermal boundary conditions. The two aluminum or

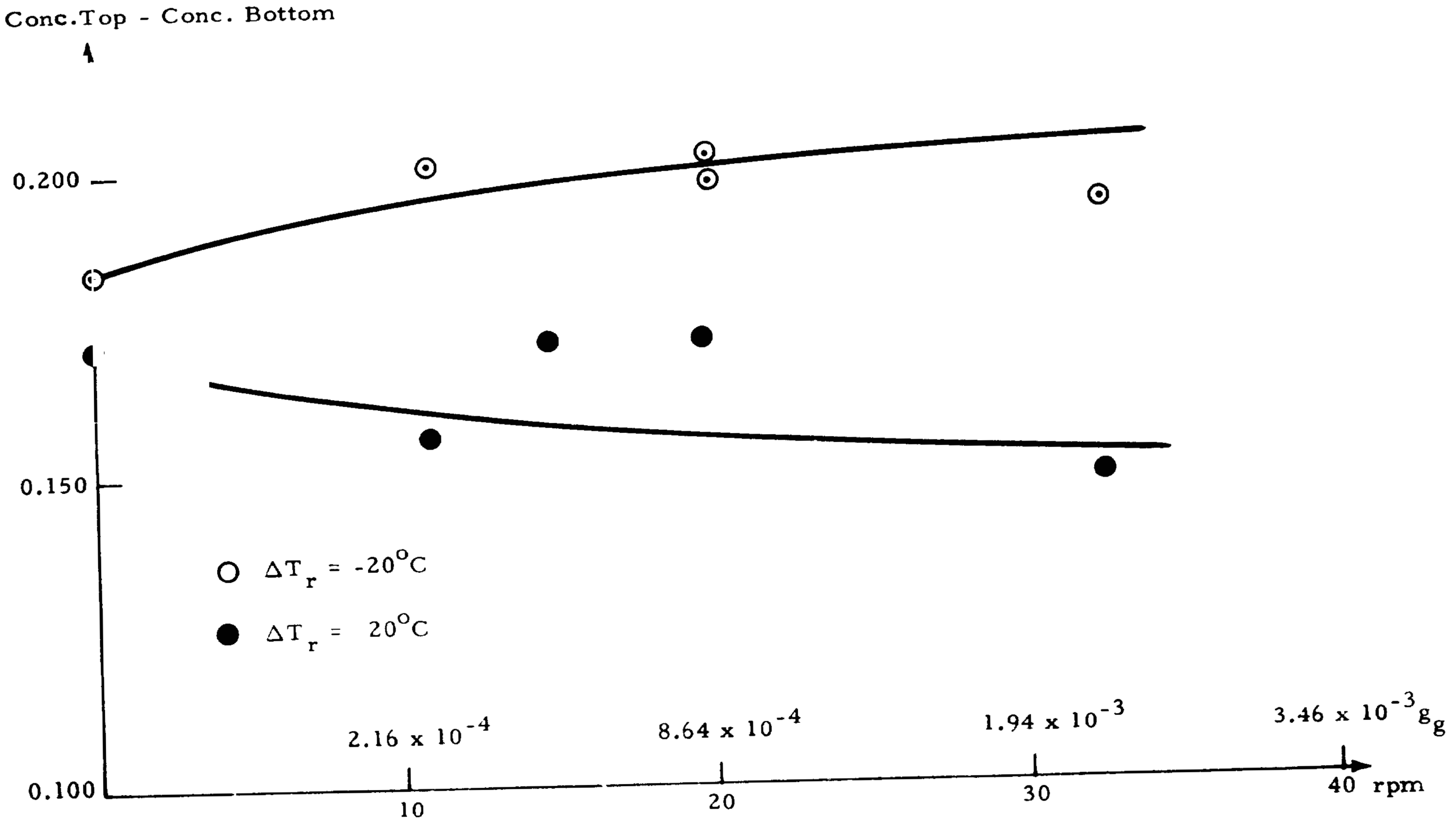
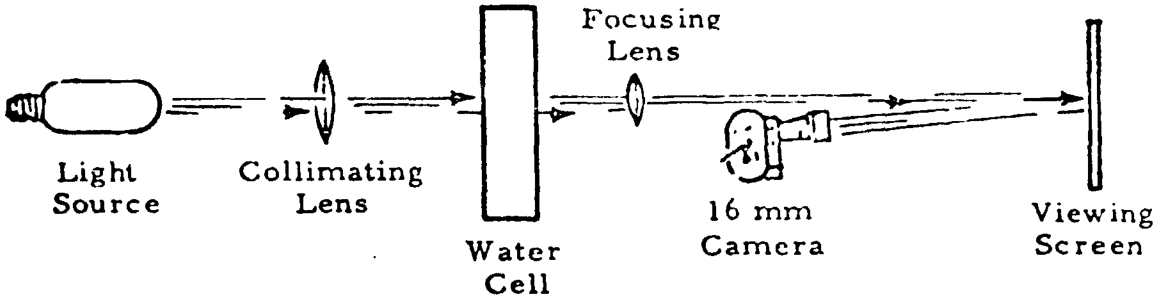


Fig. E5 - Separation in a Rotated Column of 0.0508 cm Wall Spacing stainless steel surfaces were fitted with water jackets for differential heating and cooling. The temperatures of the hot and cold surface of the test cell were monitored by copper-constantan thermocouples. Water was used as the working fluid during these tests.

Two methods were used to visualize the flow. The first consisted of mixing small aluminum particles in the water. The convective currents could then be viewed through the plexiglass sides. The second technique used was an optical shadowgraph system. A schematic of the shadowgraph is shown below.



With this system one can view on the screen directly changes in density gradients for natural convection flows. The addition of particles is suitable for determining conditions which generate multicells but cannot be used during separation tests.

Several experiments were run to determine if multicellular convection flows could be generated in the test cell. The preferred mode for a box in the vertical position heated from the side is unicellular, however, as the Rayleigh number is increased secondary flows are generated. For our test cell, at the largest ΔT that could be maintained, $40^{\circ}C$ and $Ra = 6 \times 10^6$, only the unicellular flow could be observed. Multicells are generated in a horizontal box heated from below (Ref. E-2), however, this configuration does not generate the movement parallel to the hot and cold sides needed for thermal separation. A solution to this problem is to incline the cell from horizontal while still maintaining multicell flow patterns. Table E-4 shows the results of experiments in which the test cell was inclined from the horizontal position. A disadvantage of this technique for water is that only a fairly small temperature difference can be maintained or the flow will go turbulent. Turbulence must be avoided in thermal separations since it will cause remixing to occur. From these tests, it was shown that a 25-degree inclination from horizontal laminar, multicellular convection could be maintained in the test cell along with a reasonable unicellular outer flow. Inclining above 25 degrees produced only unicellular flow patterns.

Table E-4

FLOW PATTERN AS FUNCTION OF INCLINATION ANGLE OF FLAT PLATE CELL

Inclination from Horizontal (deg)	Type of Flow	ΔT (^{o}C)	Rayleigh Number
5	Multicell-Laminar	5	4×10^5
5	Multicell-Turbulent	9	7×10^5
21.8	Multicell-Laminar	5	4×10^5
25.4	Multicell-Laminar	5	4×10^5
30.1	Unicell-Laminar	5	4×10^5
30.1	Unicell-Turbulent	10	8×10^5

Another means of controlling the flow pattern possibly is by packing. A number of papers in the literature indicate that packing reduces convective velocities. By packing, therefore, the onset of turbulent convection can probably be delayed enabling higher temperature differences to be utilized. Higher temperature differences could also be utilized in low- environments. In the tests conducted during the present study, both packed and unpacked cells were studied. Table E-5 summarizes the experimental tests accomplished with the flat plate cells.

Table E-6

SUMMARY OF EXPERIMENTS WITH VERTICAL FLAT PLATE CELLS

Cell	Test Solution	d (cm)	Rayleigh No.	Flow Pattern	Cell Position	Separation in 120 hours
A	0.15 M sucrose	2.54	5×10^5	Unicell	Vertical	None
				Multicell	Inclined 23°	None
A packed with glass wool		1		Probably Unicell	Vertical	None
				?	Inclined 23°	None
B	0.1 M copper sulfate	1	5×10^4	Unicell	Vertical	None
				Multicell	Inclined 23°	None
B packed with glass wool				Probably Unicell	Vertical	None
				?	Inclined 23°	None

The results as can be seen are inconclusive. The temperature differences in these studies were probably too small. Unfortunately, time did not permit exploring higher ΔT values in the packed cells.

REFERENCES

E-1. Harner, H. A., and M. M. Bellamy, "Applications for Liquid Thermal Diffusion," Am. Lab., January 1972, pp. 41-44.

E-2. Stock, K., and W. Muller, "Convection in Boxes," J. Fluid Mech., Vol. 54, 1972, pp. 599-611.

Appendix F
SUMMARY OF NUMERICAL ANALYSES STUDIES

Appendix F

The numerical modeling of a CD cell was explored very briefly. It was anticipated that a numerical analysis would undoubtedly be a difficult and complicated task and, therefore, beyond the scope of the present stu However, it was of interest to identify the types of difficulties that would encountered and to determine if they could be readily circumvented to yield useable results. The impetus for this work was the difficulties noted in the experimental work of identifying the boundary conditions for generating multicellular convection. Also, Lockheed had already on hand a convection program (the Lockheed Convection Analysis Program (LCAP) which had been used to successfully analyze a number of low-g and one-g convection problems. A few exploratory runs, therefore, could be undertaken as a minor task under the total study.

The determination of the flow, thermal, and concentration fields in a CD cell requires the simultaneous solution of the Navier-Stokes equations, the energy equation, and the species equations. In the LCAP the Navier-Stokes equations are used in primitive form rather than invoking transformations or change of variables. The equations are modified to include a modified Boussinesq equation of state. A binary mixture is assumed such that only one specie equation needs to be considered. The numerical algorithm proceeds as follows:

1. The energy equation is solved to yield the temperature distribution.
2. The modified Boussinesq equation then yields the density profile.
3. The momentum equations are solved to yield the flow rate.
4. The specie equation yields the concentration profile.

5. The global continuity equation is then solved for the overall mass balance in the system.
6. The process is repeated for each time step until a steady state is reached.

Values of the Soret coefficient are of the order of magnitude of 10^{-3} to 10^{-5} reciprocal degrees both in gaseous and liquid mixtures. This fact implies that the thermal diffusion term in the specie equation may have little effect on the flow and the thermal fields. Consequently, for the interest of saving computation time, one may obtain the steady state thermal and flow fields by just considering the Navier-Stokes equations and the energy equation. With the known thermal and flow fields one can then solve the specie equation for concentration distribution.

The modified program was applied to the case of a cylindrical column shown in Fig. F-1. The cylindrical annulus was filled with a 5% copper sulfate water solution initially at 304°K. The ends of the column were insulated. The inner cylindrical surface was heated to 334.4°K while the outer surface was cooled to 273.6°K. The gravity level was assumed to be 10^{-3} of the earth gravity.

Our numerical results show that for the 5% copper sulfate water solution in the said cylindrical column, steady state temperature and velocity fields prevail for $T > 50$ sec. However, the concentration field is essentially the same as the initial state.

An examination on our results shows that, at the selected g level (10^{-3} of earth gravity), the steady state temperature distribution is essentially governed by one-dimensional heat conduction only. Except for regions very close to the ends of the column, the u-velocity is less than the v-velocity by an order of three or more. This suggests that, for a column in low-g environment, the one-dimensional flow model is realistic. The temperature map is shown in Fig. F-2. It is seen that the isotherms are all straight lines Shown in Fig. F-3 is the flow map. It is clear that the flow is essentially one-dimensional except the regions very close to the ends of the column.

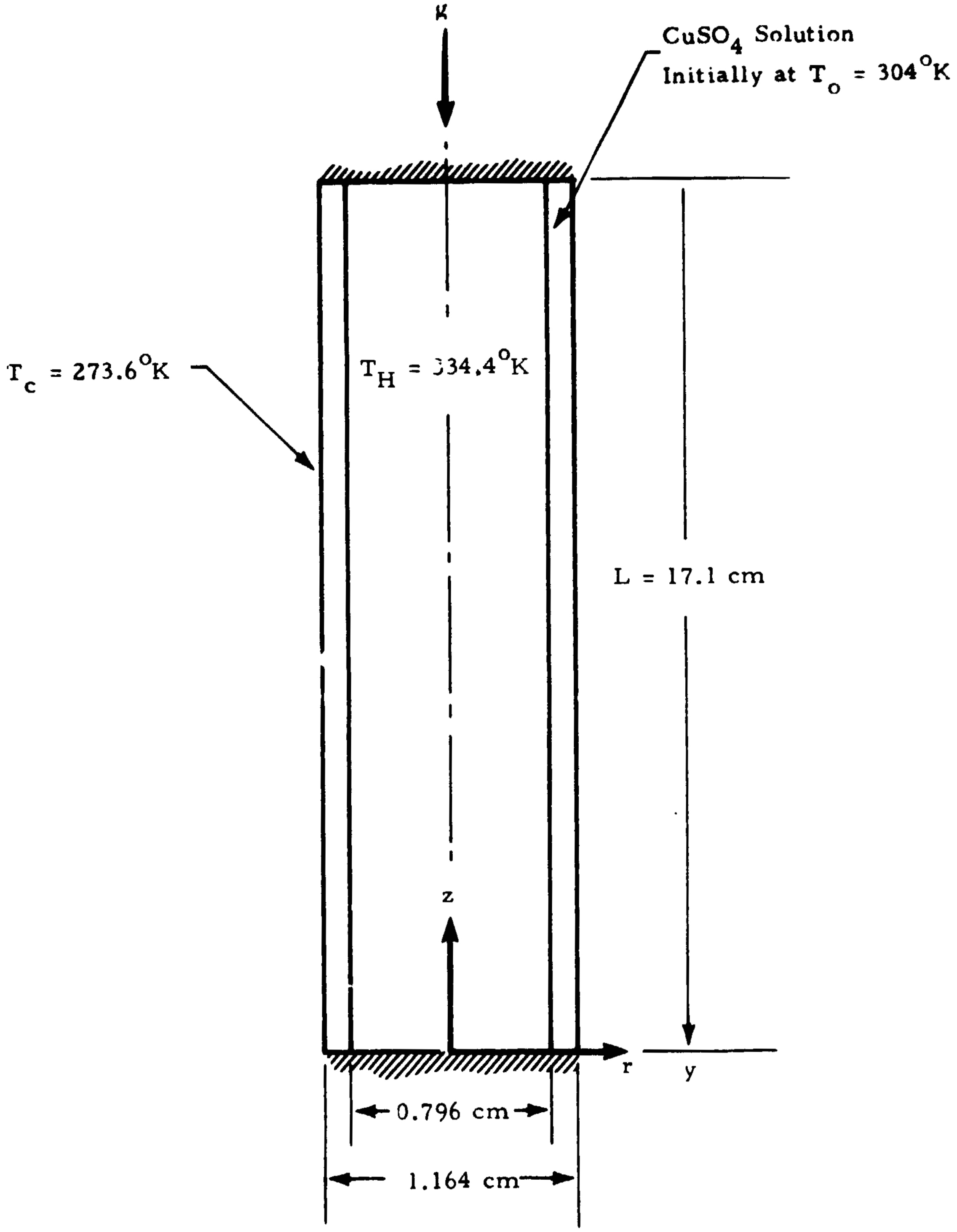


Fig. F. 1 - The Cylindrical Diffusion Column

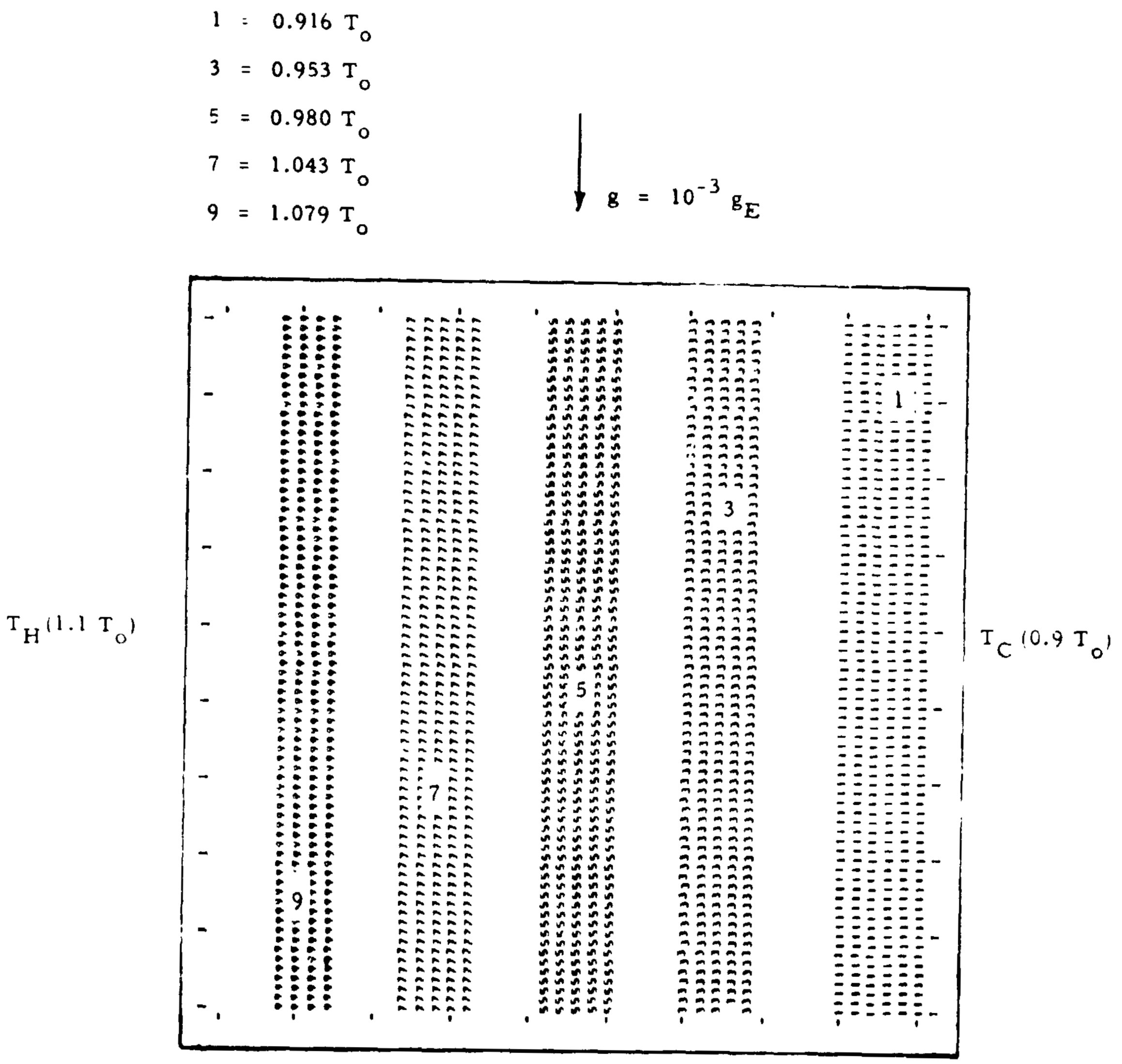


Fig. F-2 - Temperature Map

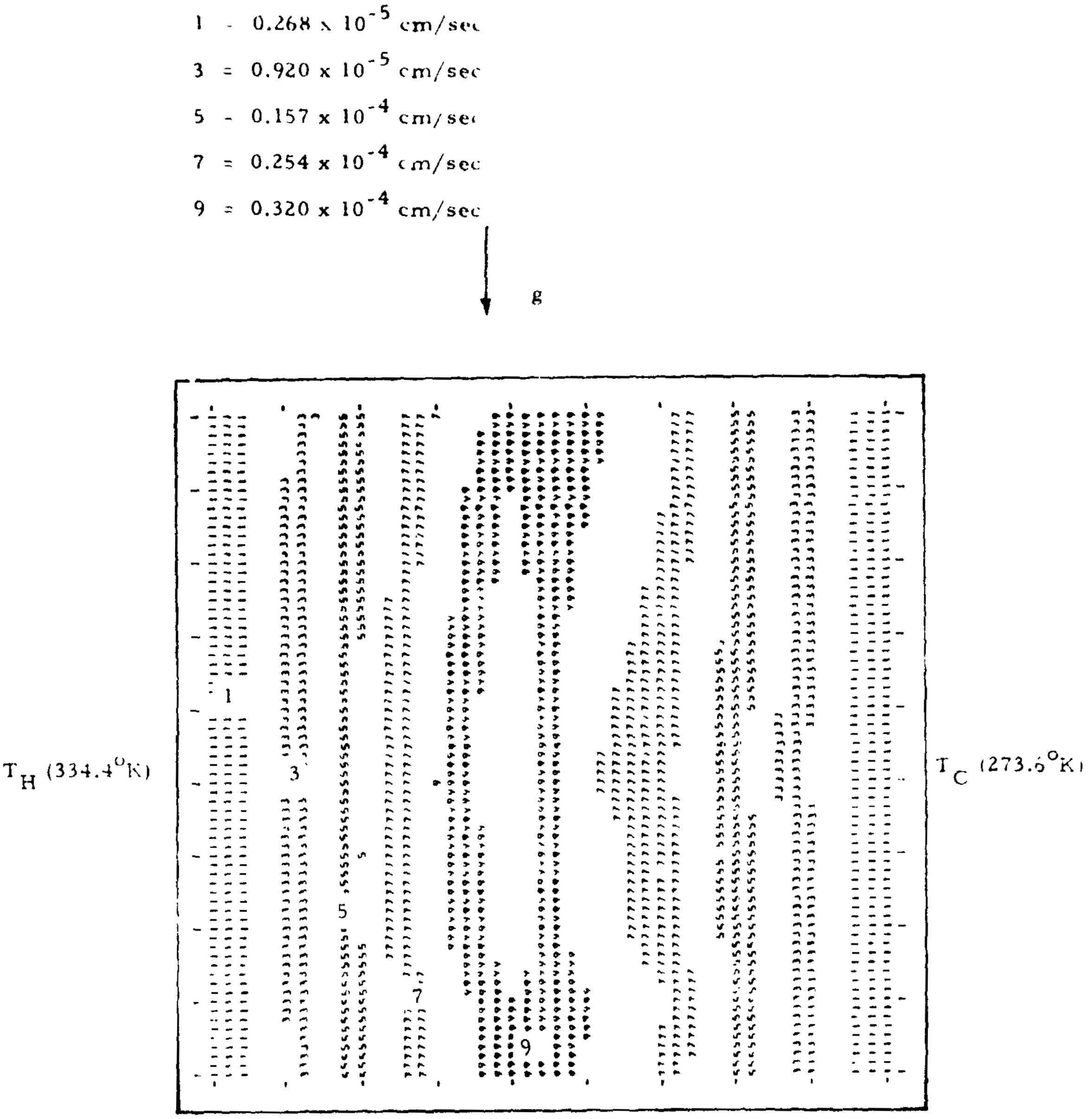


Fig. F-3 - Flow Map

The v-velocity distributions at z = 0.05L, 0.45L, and 0.95L are displayed in Fig. F-4. Also shown in Fig. F-4 is the velocity predicted by one-dimensional model. The model is seen to be, as we expect, realistic.

With the velocity and the thermal fields known, we could proceed to solve the specie equation. The concentration map at t = 14 hours is shown in Fig. F-5. It is seen that more $CuSO_4$ are accumulated at the bottom of the column. However, the concentration in the column is everywhere greater than the initial value! This is physically impossible and is mainly due to the numerical error.

The difficulties discovered with a numerical analyses of CD are determined to lie in the areas of numerical stability and finite-difference non-conservation. The numerical solution of the binary specie equation was not obeying strict conservation of mass and computation truncation errors grew in magnitude. This resulted in an invalid solution for the concentration profiles. The basic problem arises because of the large number of time iterations required to achieve a steady state for the slow processes of CD or thermal diffusion.

Recommendations

From this brief study, it is concluded that a numerical solution of the CD problem is feasible with current technology; however, such a computer program cannot be successfully developed as a "sidelight" of another type of effort. A specific study should be undertaken to develop a finite-difference solution of the "conservation" form of the binary species equation and then to couple the effects of concentration gradients of the buoyant forces. This will allow each specie to be exactly conserved in a confined region such as an annulus. In addition, a time-scale algorithm should be developed to scale the thermal diffusion time to the same magnitude as the bulk fluid flow (convection) characteristic time. This will result in a very efficient solution in terms of computer costs and feasibility. These new features can then be coded as subroutines and added to the LCAP code. Solutions for real CD

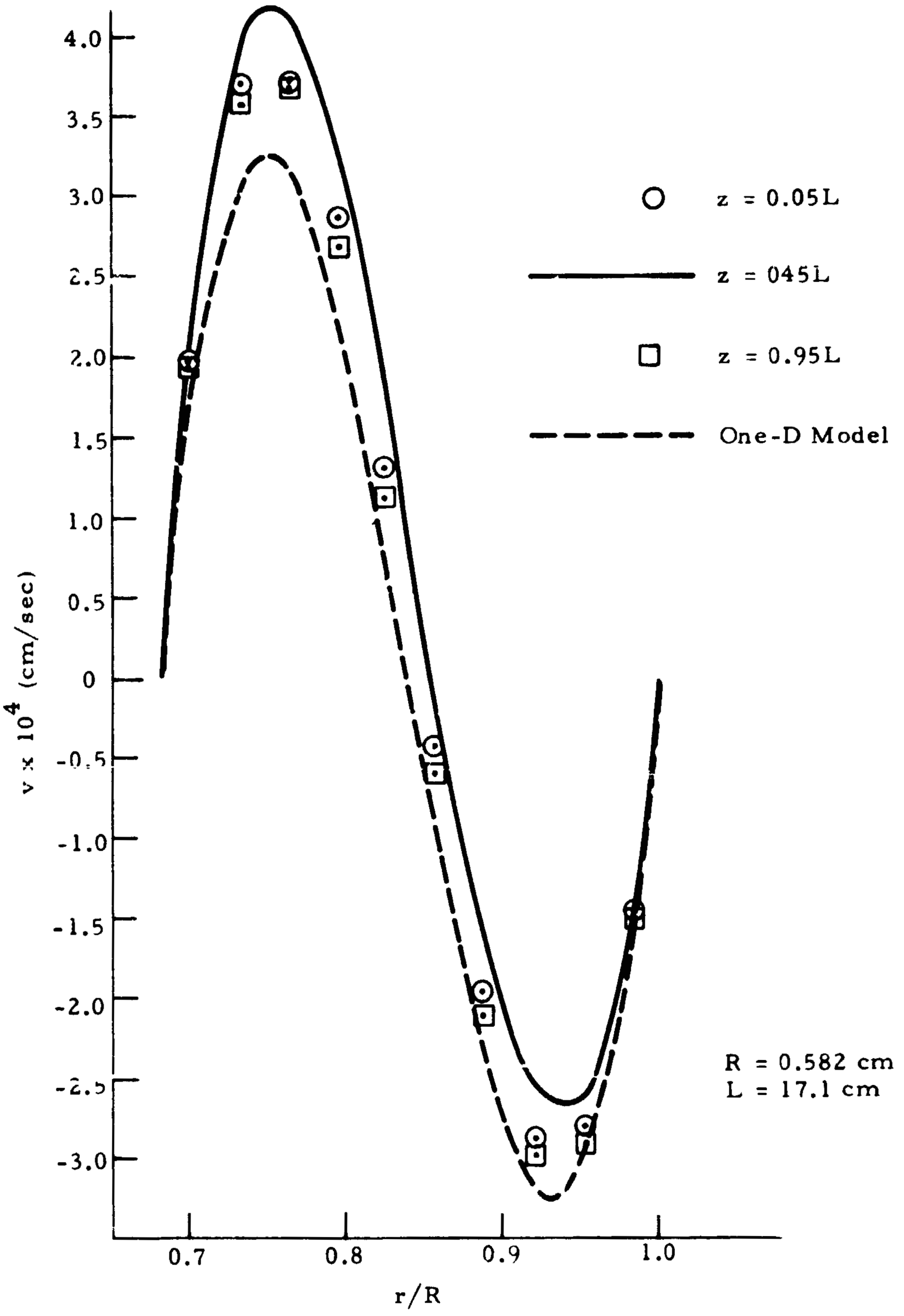


Fig. F-4 - V-Velocity in the Column

Mole Fraction

1 0.1362

3 = 0.1948

5 = 0.2536

7 = 0.3415

9 = 0.4002

$C^o = 0.05$

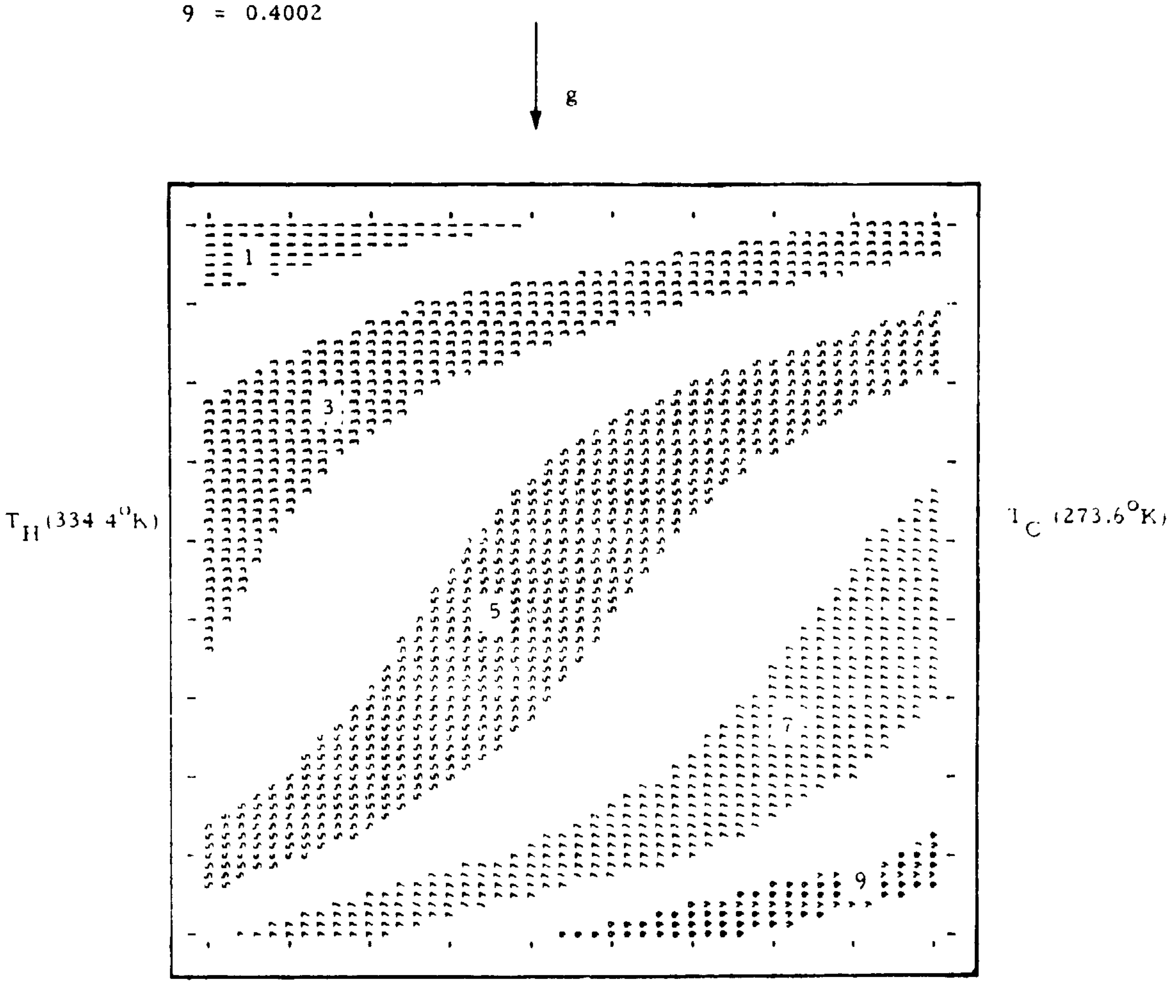


Fig. F-5 - Concentration Map (Time = 14 hours) separation problems can then be analyzed (at any gravity level) and the results compared to experimental data. On the basis of the brief study made in this work, it is believed that development of this type of computer program is feasible and would be useful as an aid in further understanding and applying CD separation processes.

Appendix G

DIFFUSION COEFFICIENTS AND CONCENTRATION UNITS AND OTHER NOTES

Appendix G

Newcomers to the field of CD separation can become easily confused because investigations conducted on gases have employed fraction, volume fraction, and weight fraction units, while investigations dealing with liquids have generally utilized molar or molal units. It may be worthwhile to mention, therefore, that the value of the diffusion coefficient is dependent on the units used for concentration. The dependence of diffusion coefficients on units used for concentration can be seen from consideration of the following relationships:

Molefraction Units $J_{c_1} = n M\,Wt_1 D_c \frac{\partial c_1}{\partial x}$ (gm/cm^2-sec)

where n is the total number of moles per unit volume.

Weight Fraction Units $J_{w_1} = \rho D_w \frac{\partial w}{\partial x}$ (gm/cm^2-sec)

Molar Concentration Units $J_{m_1} = M\,Wt_1\, D_m \frac{\partial m_1}{\partial x}$ (gm/cm^2-sec)

where the J terms are diffusional fluxes. By performing a set of simple mathematical operations, an example of which is subsequently given, relationships of the form

$$D_c = D_m \left[1 + \frac{\partial \ln \rho}{\partial \ln c_1}\right]$$

can be readily obtained. It is also useful to know that

$$q = \frac{c_e(1 - c_s)}{c_s(1 - c_e)} = \frac{w_e(1 - w_s)}{w_s(1 - w_e)}$$

Example Conversion of D_m to D_c

Let

$$m_1 = \frac{\text{moles } 1}{V}$$

and

$$c_1 = \frac{\text{moles } 1}{\text{moles } 1 + \text{moles } 2}$$

and

$$\rho = \frac{\text{grams } 1 + \text{grams } 2}{V}$$

Therefore,

$$m_1 = c_1 \left(\frac{\text{moles } 1 + \text{moles } 2}{\text{grams } 1 + \text{grams } 2} \right) \rho$$

$$\frac{\partial m_1}{\partial x} = \rho(\quad)\frac{\partial c_1}{\partial x} + c_1(\quad)\frac{\partial \rho}{\partial x}$$

$$= \frac{m_1}{c_1}\frac{\partial c_1}{\partial x} + \frac{m_1}{\rho}\frac{\partial \rho}{\partial x}$$

Furthermore,

$$n\,M\;Wt_1\,D_c\frac{\partial c_1}{\partial x} = M\;Wt_1\,D_m\frac{\partial m_1}{\partial x}\,,$$

$$n\,M\;Wt_1\,D_c\frac{\partial c_1}{\partial x} = M\;Wt_1\,D_m\left[\frac{m_1}{c_1}\frac{\partial c_1}{\partial x} + \frac{m_1}{\rho}\frac{\partial \rho}{\partial x}\right]$$

$$n\,M\;Wt_1\;D_c = M\,Wt_1\,D_m\,\frac{m_1}{c_1}\left[1 + \frac{\partial \ln \rho}{\partial \ln c_1}\right]$$

$$D_c = \frac{m_1}{n\,c_1}\,D_m\left[1 + \frac{\partial \ln \rho}{\partial \ln c_1}\right]$$

$$D_c = D_m\left[1 + \frac{\partial \ln \rho}{\partial \ln c_1}\right]$$