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REVIEW

Clusius-Dickel Separation: A New Look at an Old Technique

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Abstract

The Clusius-Dickel (CD) technique couples thermal diffusion to a countercurrent, natural convective flow to effect separation of molecules of different molecular weights or shapes in liquid or 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, and gas mixtures including ortho- and para-hydrogen.

The technique was discovered in the late 1930s by K. Clusius and G. Dickel but fell into relative obscurity for commerical 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 Clusius-Dickel separation (CDS) technique, concludes that the objectionable features of the technique can probably be circumvented by a number of means among which are: utilizing modified cell designs; combining the CD technique with other separative techniques or principles, i.e., electrophoresis, field flow fractionation (FFF), adsorption (parametric pumping), or chemical reactions; and conducting the CD operation in space environments. The first two means 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. Furthermore, the CD principle appears to offer novel

applications such as solar water desalination, energy conversion devices, and a use for waste heat.

In addition to presenting the mentioned critical reexamination and potential applications, the present document reviews the history and theoretical basis of the technique.

INTRODUCTION

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 1911–1912 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. 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 (*1*). Therefore, separations in static cells, i.e., cells in which no fluid flow occurs, have never 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 m long, Clusius and Dickel increased the separation of $H^{35}Cl$ from $H^{37}Cl$ by a factor of 4000 over that obtainable in a nonconvective cell. Separation of a large variety of materials was investigated soon after announcement of the discovery.

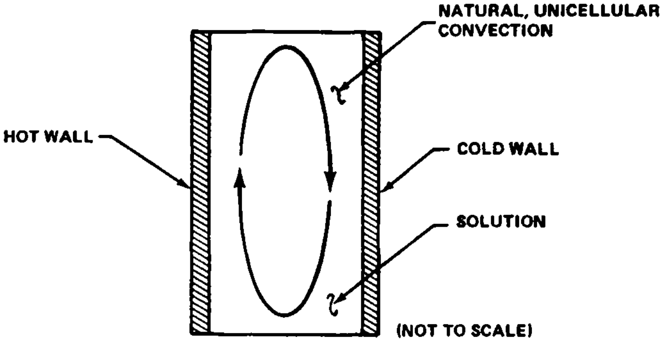


FIG. 1. Schematic of CD cell essentials.

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 coaxial cylinders. The essential elements of an apparatus illustrating the principles involved are shown in Fig. 1.

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, is opposed by ordinary mass diffusion. 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 because of thermal diffusion are removed faster in the vicinity of the wall than they are near the center of the cell by downward or upward flowing currents. Back mass diffusion is thereby reduced. The faster rate of removal near the walls than in the center of the cell is a consequence of the flow velocity profiles generated by a unicellular, natural convection (see Fig. 2). If convection is too fast, however, a remixing effect due to flow can predominate. Obviously, an optimum flow rate or convective velocity exists.

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 wartime security the work was highly secret and publications did not appear until after the war. In publications appearing after the war it was reported that a plant had been constructed as part of the Manhattan

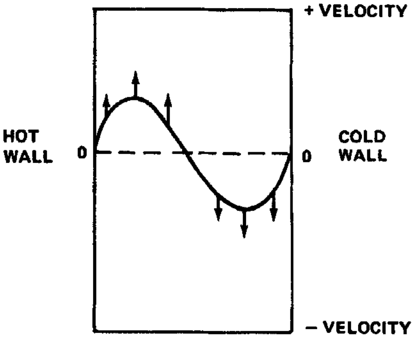


FIG. 2. Schematic illustrating velocity profile of convection in a CD cell.

project which enriched normal uranium containing 0.715 % ^{235}U to 0.86 %. The plant consisted of 2100 separation columns, each about 48 ft long. The uranium was processed as uranium hexaflouride. The plant was in operation for about 6 months and then was dismantled when CDS was displaced by the gaseous diffusion enrichment method. The principal drawback of conventional CDS for uranium enrichment is the generally low efficiency resulting in a 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 (*2*).

During the 1950s the technique was explored for various separations and fractionations of petroleum and associated products (see the next section for specific separations). Because of the high power requirements, however, this area of application also faded. As far as is known, CDS is presently utilized commercially only for the separation of rare gaseous isotopes and for purification of inertial guidance fluid. It may be mentioned incidently that CDS is also referred to as "thermogravitational separation" in the literature. More extensive historical disussions of both the CDS technique and the Soret effect will be found in the general references given in the Bibliography.

Although CDS is currently a relatively obscure technique, a number of papers on the topic have recently appeared. It is interesting to note that the Russians are responsible for some 10 of the recent papers on the CD technique (see Bibliography). A number of papers also have appeared dealing with the role of the Soret effect in phenomena such as thermosolutal convection and crystallization. It would thus appear that a general resurgence of interest in CDS and in the Soret effect is imminent.

The present study derived its motivation from the NASA program called Space Processing. The Space Processing program has as one of its objectives the definition of space processes that will result in unique or better products than are possible on earth. The primary purpose of the present study was to determine if CDS would generally be benefited by low gravity environments. In the sections that follow a consideration of topics relevant to answering the question of space processing benefits is presented. Also considered are topics which, it is hoped, will awaken the interest of scientists to the as yet unexplored possibilities and potentialities of the CD technique for earth as well as space applications.

MATERIALS SEPARABLE 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.

As is subsequently discussed, one of the chief determinants of separation by thermal diffusion is the thermal diffusion factor (or the Soret coefficient). 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
Aqueous electrolytic solutions
Aqueous nonelectrolytic solutions
Polymer solutions
Organic isomers
Binary and ternary organic mixtures
Oil fractionations
Isotopic solutions

Molten salt solutions
Liquid metal solutions

Gas-Phase Separation

Isotopic mixtures
Various gas mixtures
Ortho- and para-hydrogen

An extensive bibliography is given in Ref. *3* of Soret coefficients for various aqueous and organic solutions. Additional Soret coefficients and thermal diffusion factors for other type solutions are given in the following indicated references.

Polymer solutions (*4*)
Nonaqueous electrolytic solutions (*5*)
Isotopes in liquid metallic solution (*6–8*)
Various metallic solutes in liquid metals (*9–11*)
Isotopes in molten salts (*12*)
Thermal diffusion factors for some 50 gas pairs (*13*)

A multitude of separations by the CD technique therefore are possible. Specific referenced separations are presented in Table 1. The listing is

TABLE 1

Listing of Referenced Clusius-Dickel Separations (Liquid phase separations)

Biological solutions and suspensions
  Viruses and ribosomes (*14*)
  Deoxyribonucleic acid (*14*)
  Carbohydrate solutions (*15, 16*)
  Homologous fatty acids (*17*)
  Monomer and dimer unsaturated fatty acids (*17*)
  Dibasic acid esters (*17*)
  Primary and secondary amines (*17*)
  Aromatic heterocyclic amines (*17*)
  Mono-, di-, and triesters of polyols (*17*)
  Polyoxyethylene sorbital esters of resin and fatty acids (*17*)
  Fatty acids and polyol esters (*17*)
  Mono- and dicarboxylic acids (*17*)
  Alicyclic and aliphatic alcohols (*17*)

(*continued*)

TABLE 1 (continued)

- Alkyl amines and hydrocarbons and phenols and aromatic hydrocarbons (*17*)
- Methyl esters of soybean oils, mixed soybean oil esters resulting from partial methanolysis, and crude mono-, di-, and trioleate mixtures were fractionated (*17*)
- Papain and diastase solution (*16*)
- Ergosterol and cholesterol in chloroform solution (*16*)
- Casin, gelatin, egg albumin, papain, and diastase of malt solutions (*16*)

Aqueous electrolyte solutions

- $CuSO_4$ (*18*)
- CuBr (*18*)
- $CoCl_2$ (*18*)
- $ZnSO_4$ (*19*)

Aqueous nonelectrolytic solutions

- Water and 1-propanol. These compounds form an azeotropic boiling mixture (*20*)
- Water from ethyl alcohol (*3*, *21*, *22*)

Polymer solutions

- Polystyrene in toluene (*23*)
- Polymethyl methacrylate in various solvents. The separation was so rapid in this case that a CD column was not necessary (*24*)

Organic isomers

- Cis and trans isomers of 1,2-dimethylcyclohexane 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 (*21*)
- *o*-Xylene and
    - *m*-xylene (*21*)
    - *p*-xylene (*21*)
- *n*-Heptane and triptane (*21*)
- Isooctane and *n*-octane (*21*)
- 2-Methylnaphthalene and 1-methylnaphthalene (*21*)
- *n*-Pentane and neopentane (*25*)

Binary organic mixtures

- Separations achieved with:
    - 2,4-Dimethylpentane and cyclohexane. These compounds have almost identical boiling points, i.e., 80.50 and 80.74 °C (*21*)
    - An azeotropic mixture of benzyl alcohol and ethylene glycol (*21*)
    - Cyclohexane and
        - Benzene (*21*)
        - Toluene (*21*)
    - Cetane (*n*-hexadecane) and
        - Cumene (isopropylbenzene (*21*)

(continued)

TABLE 1 (continued)

        - Methylnaphthalene (*21*)
        - Benzene (*21*)
        - Toluene (*21*)
        - *m*-Xylene (*21*)
        - Mesitylene (*21*)
        - Carbon tetrachloride (*21*)
        - *n*-Heptane (*21*)
        - Decalin (decahydronaphthalene) (*20*)
    - Benzene and
        - Octadecane (*21*)
        - Hexadecane (*21*)
        - Carbon tetrachloride (*21*)
        - Cyclohexane (*21*)
        - *n*-Heptane (*21*, *22*, *26*)
        - Bibenzyl (*27*)
        - Biphenyl (*27*)
        - *trans*-Stilbene (*27*)
        - *o*-Terphenyl (*27*)
        - Diphenylmercury (*27*)
    - Cumene and methylnaphthalene (*21*)
    - Methylcylohexane and
        - *n*-Heptane (*21*)
        - Isooctane (*21*)
    - *n*-Octane and *n*-decane (*21*)
    - Toluene and
        - Chlorobenzene (*21*)
        - Methylcyclohexane (*20*)
    - *n*-Octane and 2,2,4-trimethylpentane (*20*)
    - *n*-Heptane and 2,2-dimethylpentane (*20*)
        - Cyclohexane and 2,2,3-trimethylbutane (*20*)
    - 2,2-Dimethylpentane and
        - 2,2-Dimethylbutane (*20*)
        - 3,3-Dimethylpentane (*20*)
    - 2,2,2-Trimethylbutane and ethanol (*20*)
    - Ethylbenzene and 2-ethoxyethanol. These compounds form an azeotropic boiling mixture (*20*)
        - Chlorinated aromatic hydrocarbons (*17*)
- Separations not achieved with:
    - *m*- and *p*-Xylene (*21*)
    - Benzene and cyclohexane (*20*, *21*)
    - Toluene and methylcyclohexane (*21*)
    - Cetane and cyclohexane. Separation was achieved, however, in another study (*20*)
    - Aliphatic alcohols and fatty acids (*28*)

(*continued*)

TABLE 1 (continued)

Ternary organic mixtures
- *n*-Octane, methylcylohexane, and cumene (*21*)
- *o*-, *m*-, and *p*-Xylene (*21*)
- *n*-Decane, *n*-tetradecane, and *n*-dodecane (*29*)

Oil fractionations
- White oil (*20*)
- Solvent refined, mid-continent lube oil (*20*)
- Paraffinic-type oils (*20*)
- Naphthenic-type oils (*20*)
- Mid-continent paraffin distillate (*30*)
- Furfural extract (*30*)
- Furfural extracted raffinate (*30*)
- Tall oil (*31*)
- Aromatic coal tar hydrocarbons (*17*)
- Naphthenic waxes and oils (*32*)
- Bromotrifluoroethylene telomer fluid (*33*)

Liquid phase separations	Gas phase separations
Isotopic solutions	Br_2 and Cl_2 in noble gases (*37*)
Heavy water from ordinary water (*34*)	$^{13}C^{16}O$–$^{12}C^{16}O$ (*38, 39*)
Benzene	H_2–D_2 (*40*)
C_6H_6–C_6D_6 (*35*)	T_2–H_2 (*39*)
$^{13}C^{12}C_5$–$^{12}C_6H_6$ (*35*)	^3He–^4He (*39*)
Cyclohexane	$^{12}CO_2$–$^{14}CO_2$ (*39*)
C_6D_{12}–C_6H_{12} (*35*)	$^{12}CH_4$–$^{13}CH_4$ (*39*)
$^{13}C^{12}C_5H_{12}$–$^{12}C_6H_{12}$ (*35*)	$^{16,16}O_2$–$^{16,18}O_2$ (*39*)
Carbon disulfide	^{20}Ne–^{21}Ne (*39*)
$C^{32}S_2$–$C^{32}S^{34}$ (*35*)	$H^{35}Cl$–$H^{37}Cl$ (*39*)
1-Chloropropane	Ortho- and para-hydrogen (*41*)
$C_3H_7{}^{35}Cl$–$C_3H_7{}^{37}Cl$ (*35*)	Gas pairs (*42*)
Bromoethane	CO_2–C_3H_8
$C_2H_5{}^{79}Br$–$C_2H_5{}^{81}Br$ (*35*)	CO_2–N_2O
$^{235}UF_6$–$^{238}UF_6$ (*36*)	N_2O–C_3H_8
	CO–C_2H_4
	CO–N_2
	N_2–C_2H_4
	Rare gas pairs (*43*)
	Kr–Xe
	Ar–Xe
	Ar–Kr
	Ne–Kr
	Ne–Ar
	He–Kr
	He–Xe

not exhaustive. Enough examples were chosen, however, to give a good indication of the types of separations that are feasible by the CD technique.

THEORETICAL BASIS OF CDS

Introduction

The separation parameters that are of 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

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

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 3.13.

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 1, which indicates no separation, to values in the millions or more. However, as will subsequently 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 to be 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 the following subsections.

Thermal Diffusion in Absence of Convection

The situation under discussion is typified by a cell such as shown in Fig. 3.

In the case of a bicomponent gas solution, the equilibrium separation factor for such a cell at steady state is given by the expression (*44*)

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

where c_T refers to the mole fraction of the lighter component at the top of the cell and c_B to 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 relationships

$$\alpha = k_T/c_1c_2$$

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

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.

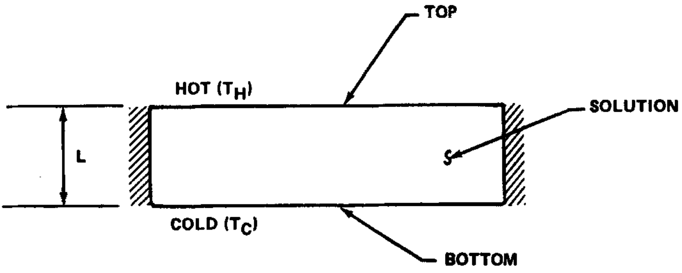


FIG. 3. Essentials of a nonconvective thermal diffusion cell.

The Soret coefficient σ is defined as

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

where D' is the liquid thermal diffusion coefficient with units of cm^2/sec-°C. The Soret coefficient is formally comparable with α/T. To obtain α from the Soret coefficient, one multiplies by the mean temperature, in °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 (*45*)

$$q_e = \frac{c_T(1 - c_B)}{c_B(1 - c_T)} = \exp\left[\sigma(T_H - T_C)\right]$$

or

$$q_e = \frac{(c_1/c_2)_T}{(c_1/c_2)_B} = \exp\left[\sigma(T_H - T_C)\right]$$

If we designate the component of smaller molecular weight as the specified component, a plus value of the Soret coefficient (or α) indicates that it will concentrate in the warm region; a negative value indicates concentration in the cold region (*3*).

As indicated by the preceding relationships, the thermal diffusion factor or constant α and the Soret coefficient σ define 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} to 10^{-3}/°C.

The relaxation time t_r' for a nonconvective cell is (*45*)

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

where L represents the distance between the plates and $A = \alpha\Delta T/2\bar{T}$, where $\bar{T}$ is the mean temperature. If the distance between the plates is small, the relaxation time is approximated by (*13*)

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

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

Cells with Convection

The mathematical treatment of Furry, Jones, and Onsager (FJO) (*44*, *46*, *47*) relating the 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 subsections a brief outline of the relationships derived from an elementary version of the FJO theory (*44*) 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 alterations required for cylindrical annulus cells, however, is indicated. The essentials of a vertical flat plate cell are shown in Fig. 4.

According to the FJO theory, the transport τ_1 of species 1 up the hot wall is given by

$$\tau_1 = Hc_1c_2 - (K_c + K_d)dc_1/dz \qquad (1)$$

where H is a term that represents the flow contributed by thermal diffusion and convection, K_c represents the remixing due to convection currents,

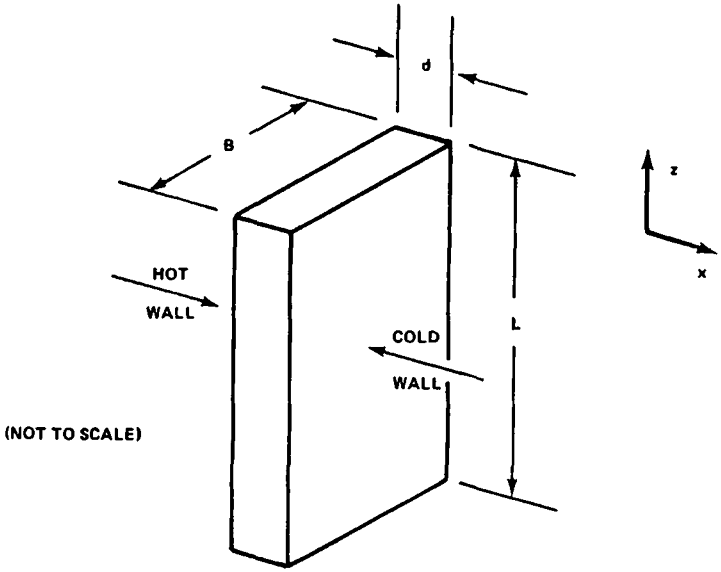


FIG. 4. Essentials of a vertical flat plate CD cell.

and K_d is ordinary diffusion back down the cell. At steady state the transport τ_1 becomes zero and Eq. (1) then yields the steady-state separation factor q_e, i.e.,

$$q_e = \exp\left[\frac{HL}{(K_c + K_d)}\right] = e^{2AL} \tag{2}$$

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

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

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

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

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

Obviously, to maximize q_e it is necessary to maximize H and minimize 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 separation spacing (d), the following procedure (*44*)

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

gives an optimum spacing of

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

and an optimum A term of

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

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

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

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

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

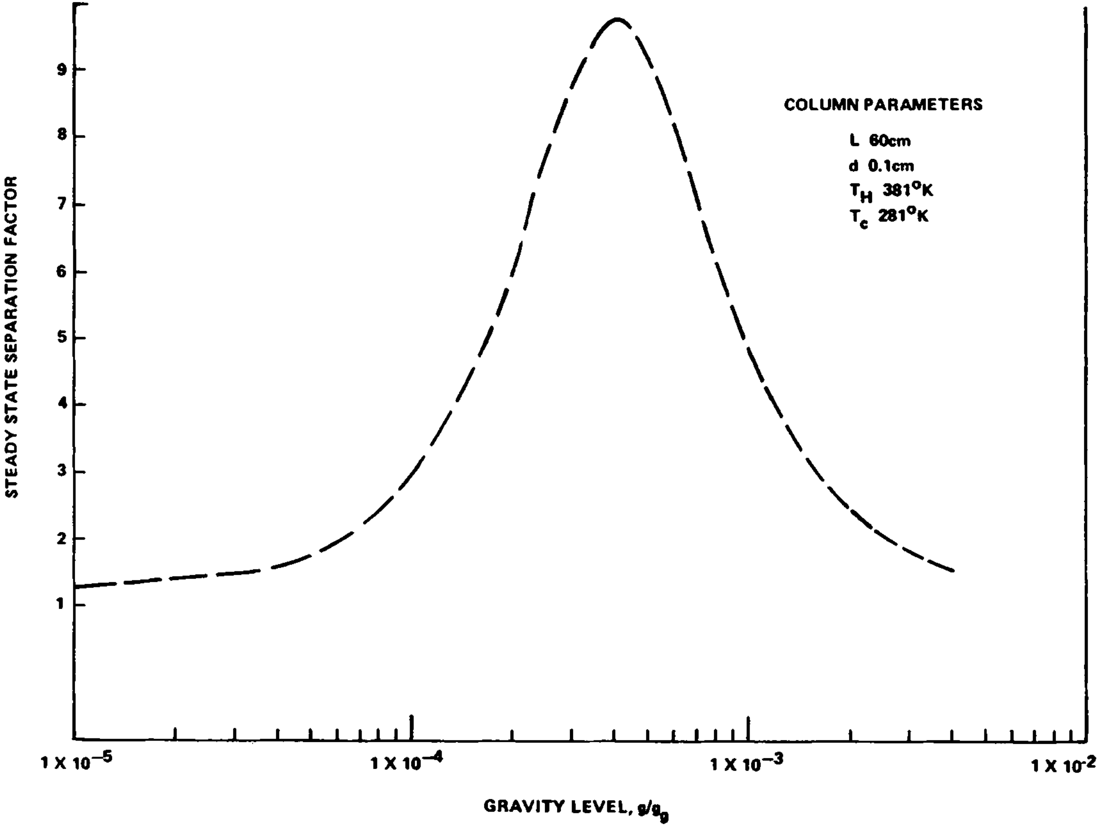


FIG. 5. Steady-state separation factor vs gravity level for the separation of ^{196}Hg from ^{200}Hg.

A sample problem of the change in q_e as a function of g level for separation of ^{196}Hg from ^{200}Hg is shown in Fig. 5.

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

$$\ln q_e = \frac{504\mu D_{12}\alpha L}{d^4\bar{\rho}\beta\bar{T}} \frac{g}{g^2 + g_{\text{opt}}^2} \tag{8}$$

When working with gases, it is also worthwhile to know the following relationship (*44*, p. 215):

$$\ln q_e = \frac{a'/P^2}{1 + b'/P^4} \tag{9}$$

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 and possible deformation on cell walls.

A relaxation time for a vertical flat plate is given by

$$t_r' = \frac{2\chi/AH}{1 + \pi^2/(AL)^2} = \frac{2\rho dB/AH}{1 + \pi^2/(AL)^2} \tag{10}$$

where χ is the mass of gas per unit length of column. Equation (10) applies only in cases where AL is rather small ($\lesssim 2$). In cases where AL is larger, a more complicated equation applies (*44*, p. 179).

The rate at which equilibrium is approached is not linear with time. In the case where AL (and $c_1 \ll 1$) is small compared with unity, the following expression gives the transient separation factor (*44*, p. 179):

$$q \sim \frac{c_e}{c_s} = 1 + 4H\left(\frac{t}{\pi\chi K}\right)^{1/2} + \cdots \tag{11}$$

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., Fig. 6, 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. *44* 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., Eq. (11), however, B remains a factor. In a case of continuous feed, which is discussed in the next section, B also cannot be ignored.

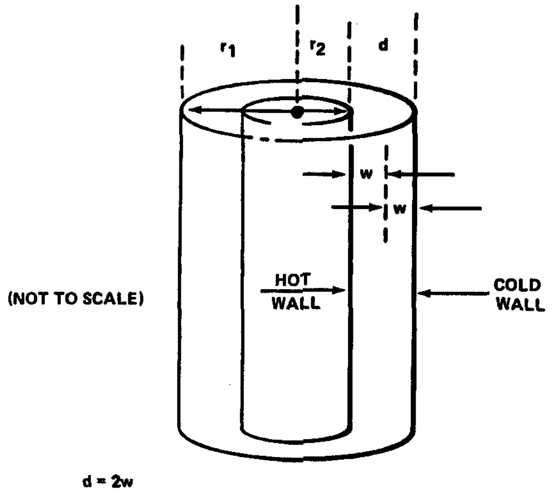
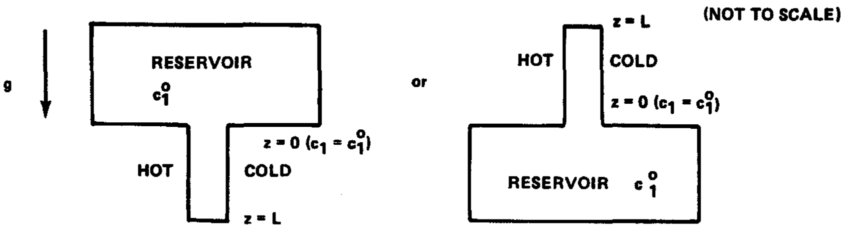


FIG. 6. Cylindrical annulus cell.

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 (see Fig. 7), c_1 at $z = 0$ remains constant at $c_1{}^\circ$. 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

$$q - 1 = (q_e - 1)[1 - \exp(-t/t_r')] \tag{12}$$



FOR MIXTURES IN WHICH THE HEAVIER COMPONENT IS TO BE SEPARATED.

FOR MIXTURES IN WHICH THE LIGHTER COMPONENT IS TO BE SEPARATED.

FIG. 7. Essentials of cells with reservoir at one end.

where t_r' is the relaxation time and can be approximated by

$$t_r' \approx \frac{\rho d B L}{H}\left(\frac{q_e - 1}{2AL} - 1\right) \tag{13}$$

In these equations it is assumed that the reservoirs are of infinite capacity and c is everywhere very small and AL is not (*44*).

Condition for Avoidance of Turbulence. In order to maintain the required unicellular flow pattern, a cell should not have parameters that would result in turbulence. Turbulence in a conventional CD cell would mean remixing and decreased separation efficiency.

Onsager and Watson (*48*) derived the approximation

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

where Re is the Reynolds number. They also showed experimentally that turbulence occurs when Re exceeds about 25.

For a CD column it can be shown by the following set of operations that the Reynolds number is equal to $2(g/g_{\mathrm{opt}})$.

$$\mathrm{Re} \cong 2\left(\frac{K_c}{K_d}\right)^{1/2} = 2\left(\frac{d^6 g^2 \bar{\rho}^2 \beta^2 (\Delta T)^2}{9!\,\mu^2 D_{12}{}^2}\right)^{1/2}$$
$$= 2\frac{d^3 g \bar{\rho} \beta \Delta T}{9!\,\mu D_{12}} = 2\frac{g}{g_{\mathrm{opt}}}$$

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

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

or

$$g/g_{\mathrm{opt}} < 12.5 \tag{15}$$

Practically, values of g/g_{opt} less than about 5 should be sought to be on the safe side. Interestingly enough, however, more efficient operation operation occurs at larger g/g_{opt} values than at smaller values (*44*).

OPERATIONAL PARAMETERS OF CONVENTIONAL CD CELLS

General Comments

As indicated previously, the theory developed in the early 1940s by Furry, Jones, and Onsager (FJO) (*44*, *47*) 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 of 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 effect 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. Also considered in this section is the effect of introducing the operational variations of continuous feed and product withdrawal and cascade design. Considerations regarding power requirements are also addressed.

Example Calculations Illustrating Single-Stage Operation

In Table 2 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 case only two types of single-stage cells are considered. One type is a flat plate cell without reservoirs. (In the preceding section 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 of cell considered is a flat plate cell with an infinite reservoir attached to the stripping end of the cell. Mathematical formulas for both types of cells are given in the preceding section. 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

TABLE 2

Example Calculations Illustrating CDS Single-Stage Operation under a Variety of Conditions

System	System type	Case	d (cm)	ΔT (°C or °K)	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 t (days)
Copper sulfate in water	Aqueous electrolytic	A1	0.721	45	30	9.88×10^{-6}	1	1780	3.2×10^{4}	39.7		
								4.4	16.4	1.8		
		A2				9.88×10^{-5}	10					
		A3				1	1.01×10^{5}	Turbulence				
		A7	2			4.63×10^{-6}	10	1.7	11.3	1.9		
		A8	0.0154			1	1					
Sugar in water	Aqueous nonelectrolytic	B1	0.013	65	30	1	1	10^{36}	10^{35}			
		B3	0.4			3.62×10^{-4}	10	3.4	130	16		
Cetane–cumene	Binary organic mixture	C2	0.686	82.2	61	3.42×10^{-5}	10	5.4	19	1.9		

Mercury— ^{196}Hg from ^{202}Hg	Metallic liquid, 1 atm pressure	D1	0.0074	100	60	1	1	10^{13}	10^{13}	8.4	1.2	Seconds
		D3	0.1			1	2.5×10^3	Turbulence				
		D5				4×10^{-3}	10	1.6	24	4.2	1.2	13
		D7	0.2			5×10^{-4}	10	1.3	22.4	4.2		
		D9			120	5×10^{-4}	10	1.6	97.3	16.7		
		D11		200	60	2.5×10^{-4}	10	1.6	24	4.2		
Sulfur—^{36}S from ^{32}S	Nonmetallic liquid	E1	0.2013	180	60	1	1	4.0	10^3	201	1.5	317
		E3	1			8×10^{-2}	10	1.06	21.8	4.3		
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			1.5×10^{-1}	1	8.6	14			
		F3				7.3×10^{-1}	5	2.3	0.6			
Uranium hexafluoride— ^{235}UF$_6$ from ^{238}UF$_6$	Liquid pressures up to 200 bars	G1	0.01104	222	1460	1	1	10^{16}	10^{18}			
		G2	0.025			1×10^{-3}	1	10^4	10^8		3	Seconds
		G3				1	10^3	Turbulence[a] (4.49)	(167)			

[a] See Discussion for this particular case.

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 2 are given in Table 3. It may be noted again that the cell width B cancels out in the steady-state equations used for the Table 2 calculations.

One feature of the calculations presented in Table 2 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 a following section.

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, temperature difference, and column length in Case G3 are those which were used in producing ^{235}U by thermal diffusion during World War II (*49*, *36*). 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 1 g (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 2 for this case are those calculated ignoring the condition that g should not exceed g_{opt} by 12.5. 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, produced many puzzling features and inconsistencies (*50*),

TABLE 3

Material Properties Used in Calculations of Table 2

Case	Notes	Density, ρ (g/cm^3)	Viscosity, μ (poise or g/sec-cm)	Coefficient of chemical diffusion, D_{12} (cm^2/sec)	Coefficient of thermal expansion, β (1/°K)	Thermal diffusion factor, a	Temperature of hot wall, T_H (°K)	Temperature of cold wall, T_C (°K)	Mean temperature, 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	353	288	320.5
Cetane–cumene	50 mole-%	0.845	5.44×10^{-3}	2.17×10^{-5}	9.46×10^{-4}	0.97	389	307	348
^{196}Hg from ^{200}Hg	Assumed isotopic abundance: 196 0.146% 200 99.854%	13.6	1.6×10^{-2}	10^{-5}	1.8×10^{-4}	0.03	381	281	331
^{36}S from ^{32}S	Assumed isotopic abundance: 32 99.9864% 36 0.0136%	1.81	186	10^{-5}	4.3×10^{-4}	0.03	573	393	483
$^{13}CH_4$ from $^{12}CH_4$	Assumed 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 $^{238}UF_6$	Assumed isotopic abundance of uranium: 235 0.71% 238 99.29%	2	7×10^{-3}	2×10^{-5}	1×10^{-3}	0.005	559	337	448

arising undoubtedly from deviations from a strictly unicellular flow pattern. In a following section the effect of flow patterns on separation efficiency is considered further.

Another aspect of CDS that emerges from consideration of Table 1 is that sizable 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 the 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 8 illustrates schematically an arrangement for continuous CD operation.

A scrubber is an additional continuous column operated as shown in Fig. 9. 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

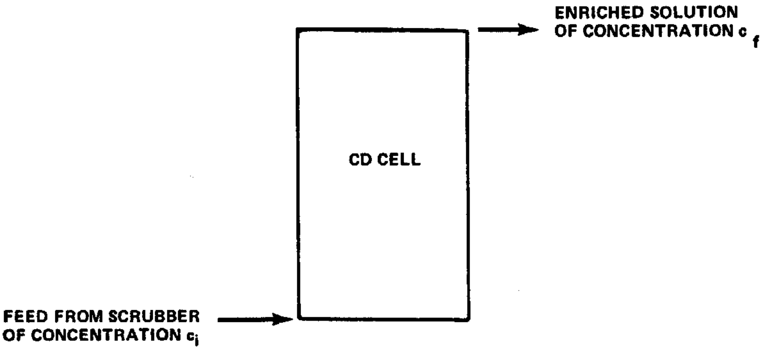


FIG. 8. Schematic of a continuous single stage CD cell.

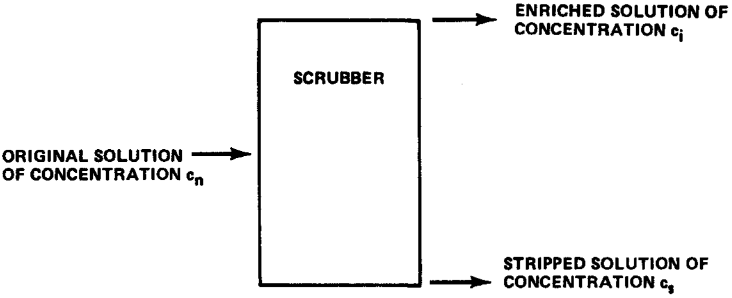


FIG. 9. Schematic of a scrubber CD cell.

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. *44*.

The effect of a continuous flow on separation in a single stage will be given by the following formula when the desired component concentration is much less than 1:

$$\frac{c_i}{c_f} = \frac{\exp\left[-2AL(1 + \sigma/H)\right] + \sigma/H}{1 + \sigma/H}$$

where σ is the flow rate in grams per second. Formulas for various other concentration ranges are given in Ref. *44*, pp. 186–187. Utilizing the preceding formula and setting σ at 1 g/day and the width of the cell at 10 cm, it is readily calculated that the ratio c_f/c_i would decrease from 1.058 to 1.057 for Case E3 in Table 2 as the result of the 1 g/day flow.

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. *44*, tables of most efficient values of σ/H and $2AL$ for various q values are given. Furthermore, it is shown in Ref. *44* that, under widely varying conditions, the most effective value of $2AL$ is given by

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

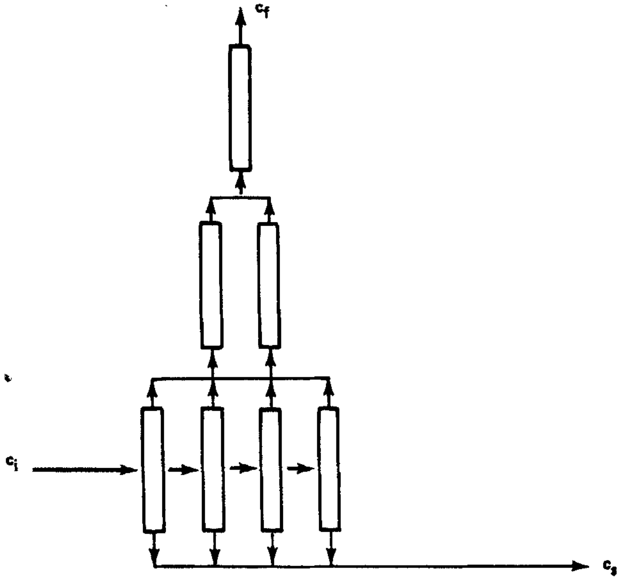


FIG. 10. Schematic of a simple cascade (*45*).

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 (*45*) is sketched in Fig. 10.

Much the same considerations as are discussed for single-stage operation apply to the multistage case. The reader is referred to Ref. *44* 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. The case of sulfur (Case E3, Table 1) is again made our reference case. Suppose we set the production rate of enriched solution at 1 g/day and the cascade construction at three stages beyond the scrubber, i.e., scrubber, 4 cells; first stage, 4 cells; second stage, 2 cells; third stage, 1 cell. A cell width (B) of 10 cm is again assumed. Utilizing the relationship for most efficient multistage operation (*44*):

$$\ln q = A\mathscr{L}$$

where $\mathscr{L}$ is the total length of the cascade (not counting the scrubber), we obtain a separation factor of 1.09. To obtain an approximate characteristic time, i.e., the time before product can start to be withdrawn at a constant rate, the following formula is applied:

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

where η_1 is the number of cells in the first stage. For the conditions defined here, t_c is calculated to be 1.7 days. Thus separation can be increased from 1.06 to 1.09 and the separation times decreased from 22 to about 9.3 days by utilizing a three-stage cascade.

It is stated in Ref. *44* 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 are 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 a following section.

Power Requirements

As mentioned previously, the large amount of power required for CDS of isotopes and petroleum fractions has been the chief deterrent to commerical exploitation of the method. One experimental study of the efficiency of the method in petroleum separations (*51*) reported experimental efficiencies of about 10^{-5}. The experimental efficiency, ξ_e, is defined in the cited study by the following set of relationships:

$$\xi_e = \frac{\text{actual rate of separative work}}{\text{actual rate of heat input}}$$

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

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

TABLE 4

Comparison of Energy Requirements for Various Methods of Uranium Isotope Separation (*53*)

	Specific energy consumption (kW/kg *USW*/yr)	
Process	Theoretical minimum	Practical
CDS with UF_6	61	
Gaseous diffusion	0.073	0.266
Distillation		>0.62
Redox ion exchange		>0.71
Electromigration in UCl_4		1817
Molecular distillation		>0.073
Isotope chopper		≫0.073

terms are defined in the notation section. The experimental efficiency ξ_e can be viewed as an energy conversion efficiency (*52*). As can be appreciated, actual conversion efficiencies of conventional CDS cells are quite low. Table 4 illustrates this point dramatically. In Table 4 the energy requirements per unit separative work (*USW*) per year for various methods for uranium isotope separation are given.

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.,

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

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

$$SW = WV(c_e) + WV(c_s) - 2WV(c_f)$$

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 (*54*). Thus, a SW of 4.306 kg/hr gives 1 kg/yr of 3% ^{235}U from 5.479 kg/yr feedstock consisting of 0.711% ^{235}U (*54*, *55*).

Another study done in 1957 is of interest in connection with power requirements. Powers and Wilke (*22*) estimated the costs and power requirements for processing 1000 bbl/day of a 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} J/hr, 3.33 × 10^9 kW). It is worthwhile to mention, however, that relatively low temperatures were assumed, i.e., $T_C = -8\,°\text{C}$ and $T_H = 92\,°\text{C}$.

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 a following section.

Forgotten Effect

The fact that solution density is often a strong function of concentration was not considered in the original FJO theory. A number of peculiar column behaviors, however, were subsequently attributed to the effect of concentration on density, and the effect came to be known as the forgotten effect. The forgotten effect can affect convective flow velocity and direction and thus separation times. A reversal in flow direction may also cause a reversal in the locations of increasing concentrations, i.e., a given solution component would concentrate at the bottom instead of the expected top of the column. The forgotten effect furthermore may also cause an overturning or remixing of the separated solution if a sufficiently unstable density gradient is built up. Apparently not all unexpected reversals of concentration, however, can be attributed to the forgotten effect. A paper by Korchinsky and Emery (*56*), which appears to be the last study performed on the subject, concludes that many peculiar cases attributed in the literature to the forgotten effect were not the result of the forgotten effect but the result of minor irregularities in wall spacings.

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 (*44, 50, 57–62*). 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 (*63*). Onsager's thermodynamic efficiency for any small volume of mixture consists of the 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:

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

In energy terms the relationship is (*51*)

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

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

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

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 (*44*) determined the entropy ratio for an ideal, conventional CD cell (no asymmetries or imperfections), assuming that the product c_1c_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. *44*.

White and Fellows (*51*) 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 efficiencies. Furthermore, they concluded that the experimental efficiency of a "constant separation" cascade would be the same as for one single cell in the casade.

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 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 is less than about 0.3. In the range 0.3 to 0.7 the product c_1, c_2 is virtually constant.

One possible flow pattern which might vary the concentration appreciably along a cell is shown in Fig. 11. Cascading can have an appreciable effect on boosting separation levels, as previously discussed. The multicellular pattern shown may also be capable of sustaining internal, dynamic pressure gradients of sufficient magnitude to allow some significant pressure diffusion in addition to providing a cascading mechanism. 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 (*64*) 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. On the basis of this assertion, a simple calculation shows that a column of water 100 cm high in a gravitational field has the same separating power as a temperature

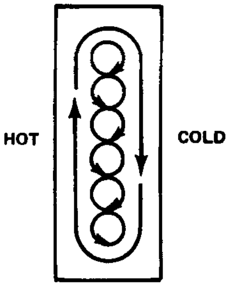


FIG. 11. Schematic of an internal cascade.

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, might not be too unrealistic. One experimental test of the possibility that small pressure gradients coupled with sustained flow can 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 types of CD cells, a rotated column was constructed, as is subsequently discussed. 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. More conclusive data, however, are required.

The present study also 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 Elder (*65*). 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 general flow patterns illustrated in Fig. 12 were observed.

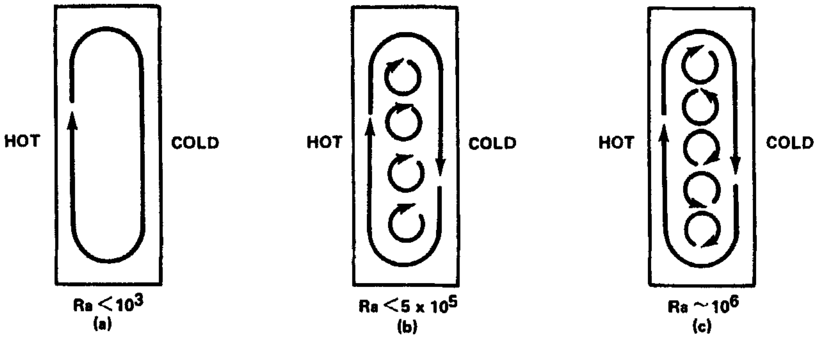


FIG. 12. Flow patterns in a thin slab as a function of Rayleigh number.

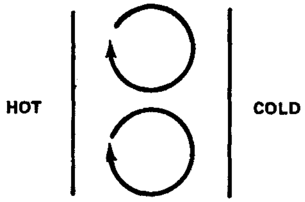


FIG. 13. Cellular pattern postulated by Cohen (*50*).

Cohen (*50*) briefly considered the effect on separation of cellular flow shown in Fig. 13. Cohen concluded that such a flow would seriously decrease separation. The present authors agree. The effect of such a flow coupled with an overall unicellular flow as is shown in Fig. 12(b), however, is not obvious. The result of a flow pattern such as shown in Fig. 12(c) 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. The difficulties encountered in experimentally identifying the conditions under which multicells are generated in a particular apparatus led to a brief exploration of a computer approach. It was anticipated that a numerical analysis would undoubtedly be a difficult and complicated task and, therefore, beyond the scope of the present study. However, it is of interest to identify the types of difficulties that would be encountered and to determine if they can be readily circumvented to yield useable results. 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) was already on hand. A few exploratory runs, therefore, were conducted.

The difficulties discovered with a numerical analysis of CD are determined to lie in the areas of numerical stability and finite-difference nonconservation. The numerical solution of the binary specie equation did not obey strict conservation of mass. As a result, 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.

From the brief study conducted, it was concluded that a numerical solution of the CD problem is feasible with current technology. A specific study, however, would have to 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 on the buoyant forces. This procedure would allow each specie to be exactly conserved in a confined region such as an annulus. In addition, a time-scale algorithm would have to be developed to scale the thermal diffusion time to the same magnitude as the bulk fluid flow (convection) characteristic time. The indicated procedure would, it is believed, result in a very efficient solution in terms of computer costs and feasibility.

Although experimental verification of multicell efficiency was not achieved in the present study, a "numbers game" given in Fig. 14 and first introduced by Grew and Ibbs (*13*) 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 also of interest to seek an answer for the question of whether rotation might affect separation by introducing a multicellular convection or by introducing an additional separating force by means of the Coriolis effect (*66*). Although a number of previous studies (*67–70*) 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 (*70*) 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 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 (*71*, *72*), 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

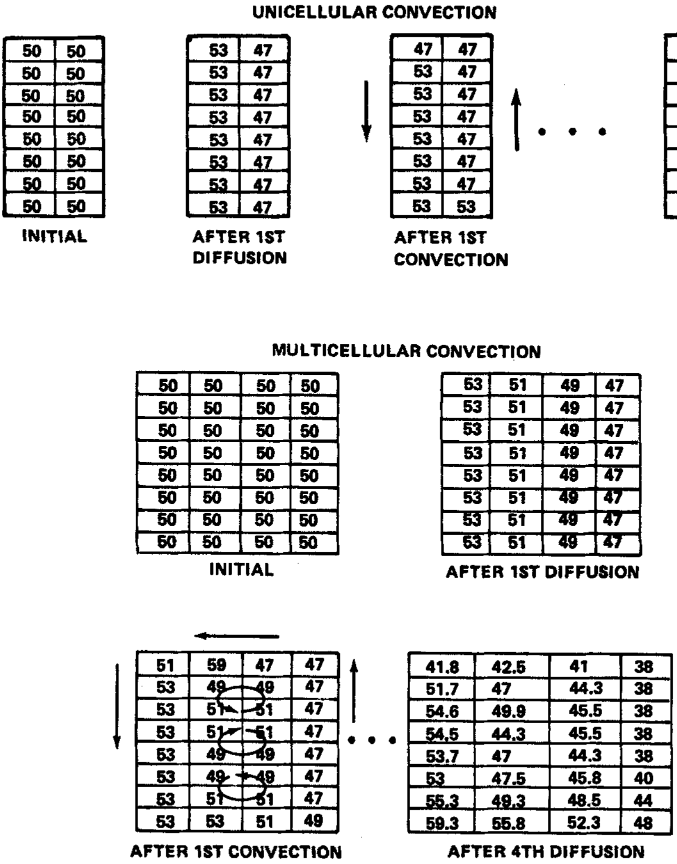


FIG. 14. Schematic after Grew and Ibbs (*13*). Illustration of concentration changes in a CD cell with unicellular and with multicellular convection. A 6% separation as the result of thermal diffusion is assumed.

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 (*73*).

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*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.

Essential features of Williams' computations have been confirmed experimentally by Koschmieder (*74*). 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.

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 futher 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, was dismissed a long time ago as being too energy costly. The matter is also important 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 efficiency would be advantageous.

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 are 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 (*75*). Most practical electrophoresis separations are conducted in the absence of free convection. Electrophoresis coupled with a forced, laminar convective flow, however, is sometimes utilized. The idea of coupling CDS and electrophoresis was inevitable. Crosser, Powers, and Prabhudesai (*76*) report the results of a study in which the apparatus utilized had the essentials shown schematically in Fig. 15.

It can be appreciated that with such a relatively complicated system it will take more than the first reported studies to adequately determine the potential of the technique. Unsurprisingly, the first study reports

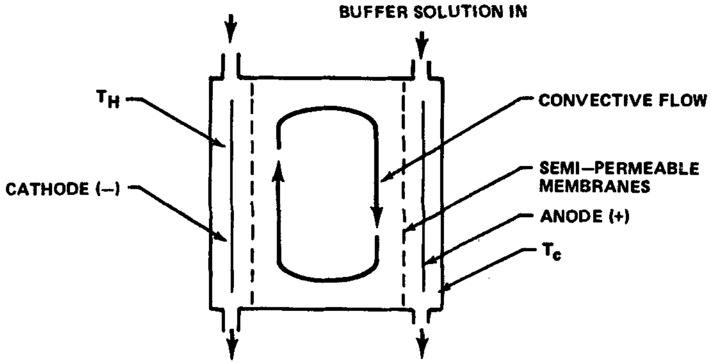


FIG. 15. Essentials of an electrothermogravitational electrophoresis column.

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, however, 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 since been 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., $^{18}O^{16}O$. At a hot surface, however, the following reaction occurs (*1*):

$$2\,^{18}O^{16}O \rightleftarrows {}^{16}O_2 + {}^{18}O_2$$

The separating effect of CD drives the equilibrium toward the right, with the result that practically pure $^{18}O_2$ is obtained at one end. Other separations reported include ^{13}C by the exchange reaction (*77*)

$$^{12}CO_2 + {}^{13}CO \rightleftarrows {}^{13}CO_2 + {}^{12}CO$$

and ^{15}N by the exchange reaction (*78*)

$$^{14}NO_2 + {}^{15}NO \rightleftarrows {}^{15}NO_2 + {}^{14}NO$$

As a method of separating isotopes, however, apparently not much advantage is realized over CDS without chemical exchange (*77*).

Hirota and Kimura (*79–82*) carried out hydrogenation and polymerization reactions of acetylene and of methane. A desulfurization reaction was also reported as having been studied (*81*). 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 essentials shown in Fig. 16 (*83*, *84*). 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.

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 conceivable that a packed CD cell already contains a mechanism for separation. Consider the CD cell shown in Fig. 17. Assume the heavier component is also the one most absorbed by adsorbent. Both thermal

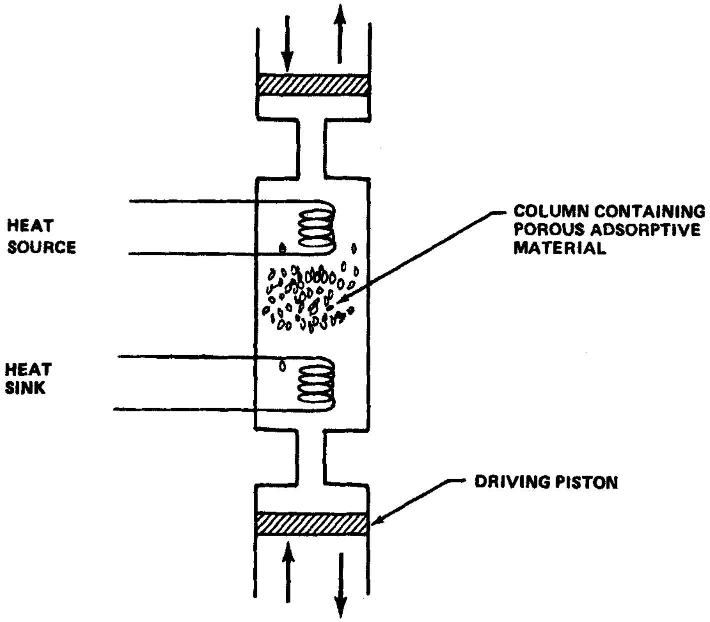


FIG. 16. Parametric pumping essentials.

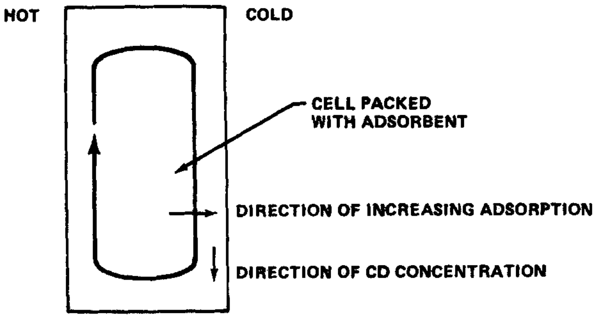


FIG. 17. Adsorption and CDS.

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, 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 hr) when the column was packed with glass wool. Table 2 shows that a 0.721-cm column could separate an aqueous copper sulfate solution to a q_e level of 4.57 in about 22 hr if the gravity level were reduced to $9.88 \times 10^{-5}\ g_g$. 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. 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 are 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 (*85*). The essentials of the technique are shown in Fig. 18 (*86*) where 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 countercurrent convective flow is introduced (*87, 88*) (see Fig. 19).

Also of interest in connection with FFF is the phenomenon of "tubular pinch effect" (*89, 90*). 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

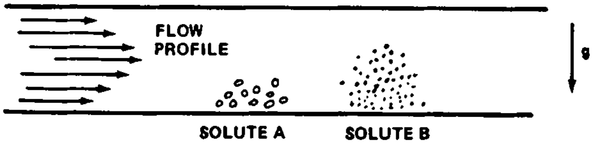


FIG. 18. Schematic of a field flow fractionation.

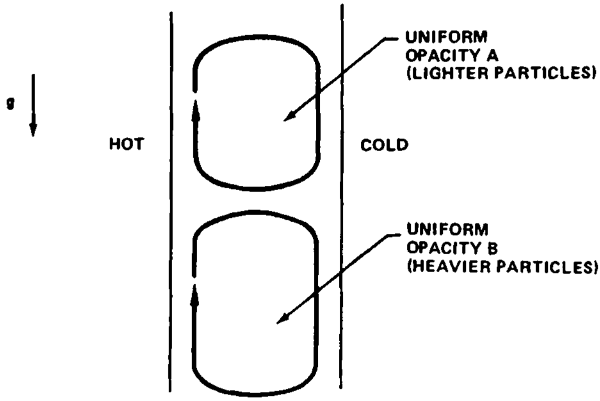


FIG. 19. Schematic of stratification sedimentation.

allied to the CD technique. In TFFF *(91)* 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 has 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, FFF, 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.

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 2. 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 1 g. These are given in Table 5.

Powers and Wilke (*22*) set a wall spacing of 0.0793 cm as a practical design limit. Commercial laboratory cells are available with wall spacings down to 0.01 cm. However, a comparison of the work of various investigators (*92*) in which d ranged from about 0.6 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 discrepancies probably arose as the result of the critical nature of the wall spacing (*92*). Other instances of anomalous or puzzling results can be cited (*49*, *93*) which also undoubtedly have their origins in small variations in the wall spacing. The present study also noted an anomalous result at a wall spacing of 0.01 cm as is subsequently discussed. Small wall spacings have the further disadvantage of smaller processing volumes. Obviously, if the wall spacing can be increased in low g, small wall

TABLE 5

Summary of Wall Spacings at Optimum g Level of 1

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

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 (*22*) 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. This case is illustrated in Fig. 20.

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. 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 (*23*, *94–101*), CD cells were packed with various packings such as glass wool and metal turning. 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, though, that packing offers an immense advantage for small batch or laboratory separations. Fairly crude cells can be used. For example, it was found in the present study that a 3% copper sulfate solution could not be separated in an unpacked cylindrical cell made of glass (0.721 cm annulus). Essentially complete separation, however, occurred in about 4 hr 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. The last section of this paper

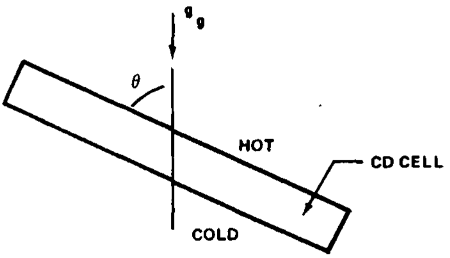


FIG. 20. Tilted flat plate cell.

gives more details for this and other separations performed experimentally 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.

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 sizable gravity gradient. Consider the gravity gradient shown in Fig. 21. 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 hot flow would encounter lesser gravity as it rises, and the cold flow would encounter greater gravity as it falls. A mathematical analysis for CDS

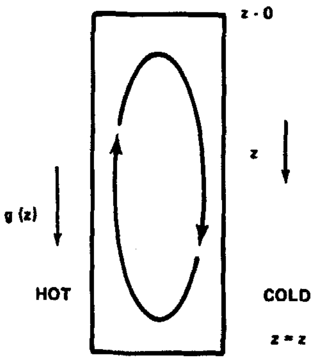


FIG. 21. Schematic showing one possible direction of a gravity gradient.

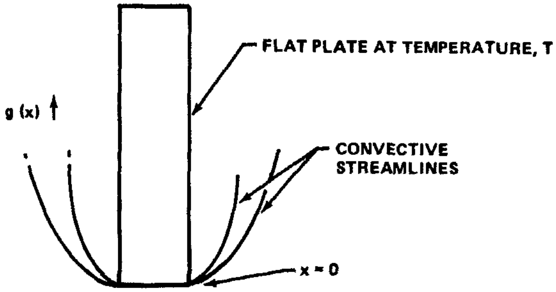


FIG. 22. Schematic of gravity gradient situation analyzed by Catton (*102*).

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. 22, in the presence of a gravity gradient (102):

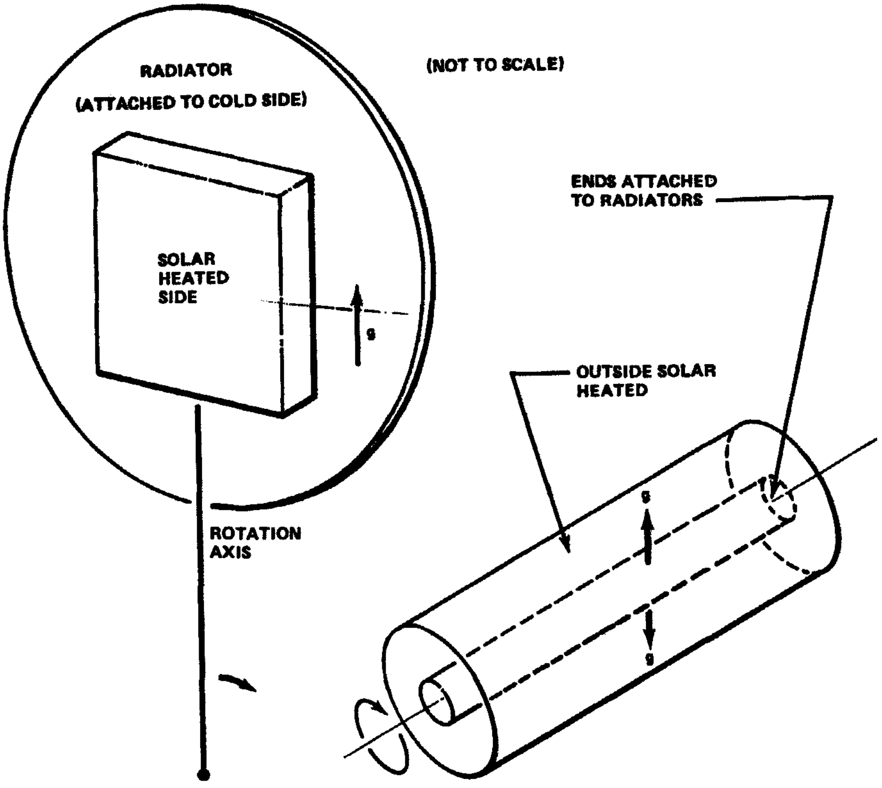
$$\frac{\mathrm{Nu}}{\overline{\mathrm{Nu}}} = 1 + \frac{7}{24}\frac{bx}{a}$$

where Nu is the Nusselt number in the presence of the gravity gradient, $\overline{\mathrm{Nu}}$ 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 $\overline{\mathrm{Nu}}$. If Nu is less than $\overline{\mathrm{Nu}}$, convective velocities 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 than $10 \times g_{\mathrm{opt}}$, allowing cell operations at gravity levels greater than $10 \times g_{\mathrm{opt}}$. It will be recalled that operation at $\sim 10 \times g_{\mathrm{opt}}$ gives greatest efficiency, i.e., most separation work in the shortest period of time. Presumably, even greater efficiency would accrue at values greater than $10 \times g_{\mathrm{opt}}$ 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 $1\ g_g$, 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 space benefit. A couple of likely concepts for accomplishing solar heating and outer space cooling are shown in Fig. 23.

With ingenuity as to the arrangement and size of focusing parabolic mirrors, a variety of temperature ranges and cell configurations can be achieved. For example, in earth orbit the solar energy intensity is of the order of 0.14 W/cm^2 or 2 cal/cm^2-min (*103*). This amount of heat would raise the temperature of a cubic centimeter volume of water 2 °C in 1 min. Thus consider, for example, a flat plate cell whose large area walls are constructed of 0.3175 cm thick stainless steel. The cell is filled with water. If the dimensions of the cell are 1 × 34.2 × 342 cm, a 2.32-



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. 23. Concepts for utilization of solar energy and space radiation cooling for CDS.

fold concentration of natural solar radiation would be required in space to maintain a 50 °C temperature difference across the 1-cm water layer. (Emissivities are assumed as 0.0 at the absorbing wall and 1.0 at the radiating wall. Absorbtivity at the absorbing wall is assumed as 1.0.) A 2.32-fold level of solar energy concentration would require a parabolic concentrator of 2.7 m^2 in area. Large concentrators in space should present no major problem, for without gravity stress aluminized plastic umbrella collectors can be utilized. Design of thermal radiators to dissipate heat at rates sufficient to maintain required temperature gradients will present more of a problem but not, it is expected, 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 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 currently sells for $880/mg (*104*). 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 (*104*).

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 6.

The fluxes indicated in Table 6 are substantially lower than those produced by nuclear reactors and particle generators such as the Oak Ridge 86-in. cyclotron. The cyclotron can produce a 17-MeV proton flux of 7.8 × 10^6 particles cm^2-sec (*105*). To simulate the radiation of 23 MeV in the Van Allen belt, the cyclotron was run at a 3 particles/cm^2-sec flux density (*105*). Exposure to cyclotron radiation, however, is 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-A current to energize a 400-ton magnet, and a 4300-A 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

TABLE 6

Magnitudes of Various Radiations near the Earth (*103*)

Radiation and energy	Earth orbit flux (particles/cm^2-sec)
Protons	
0.4 MeV	10^3–10^8
4.0 MeV	10 –10^6
34.0 MeV	10 –10^4
Electrons	
>0.5 MeV	10^2–10^8
Alpha particles	
$\frac{\text{Flux of alpha particles with energy} > 2.09\text{ MeV}}{\text{Flux of protons with energy} > 0.52\text{ MeV}}$	$= 2.3 \times 10^{-4}$

1.6×10^4 neutrons/cm^2-sec, consumes 30 MW operating power (*106*). 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 if long enough 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 are 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 (*107*) 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 (*107*). The cost of radiation since Ref. *107*, 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 present attractive advantages for some processes.

EXPERIMENTAL CDS EXPERIENCES, POTENTIAL APPLICATIONS, AND FURTHER STUDIES

Experimental Studies

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: to obtain a knowledge of the practical problems involved with each type of cell; to determine the effect of small pressure gradients on separation; and to generate convective multicells and spiraling flow and to determine the effect of these flow patterns on CDS efficiencies. Details of the experimental work will not be presented here. These are documented in Ref. *108*. Noteworthy aspects of this work, however, are presented by type of column utilized.

Conventional CD Columns. 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). The essentials of the apparatus are shown in Fig. 24. Essentials of the columns provided with the Thermo-Search II are shown in Fig. 25. 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. *109*.)

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 temperatures of the hot and cold flows were either 56 ± 3 and 22 ± 2°C or 50 ± 2 and 5 ± 2°C. Separation of a series of copper sulfate solutions of 1.0 *M* concentration were studied as a function of wall spacing. The concentrations of the solutions were determined by means of an ABBE-3L Refractometer. Significant separations were achieved at the various wall spacings in times as short as 5 hr or less. The interesting result of the experiments is that the 0.1-mm wall spacing gave worst separations 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. An attempt to identify the

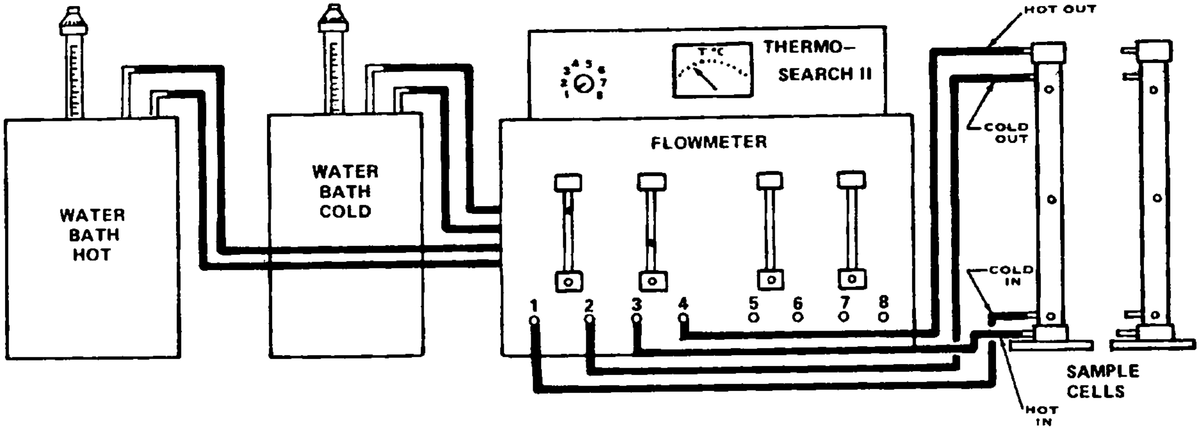


FIG. 24. Schematic of a CD separation apparatus.

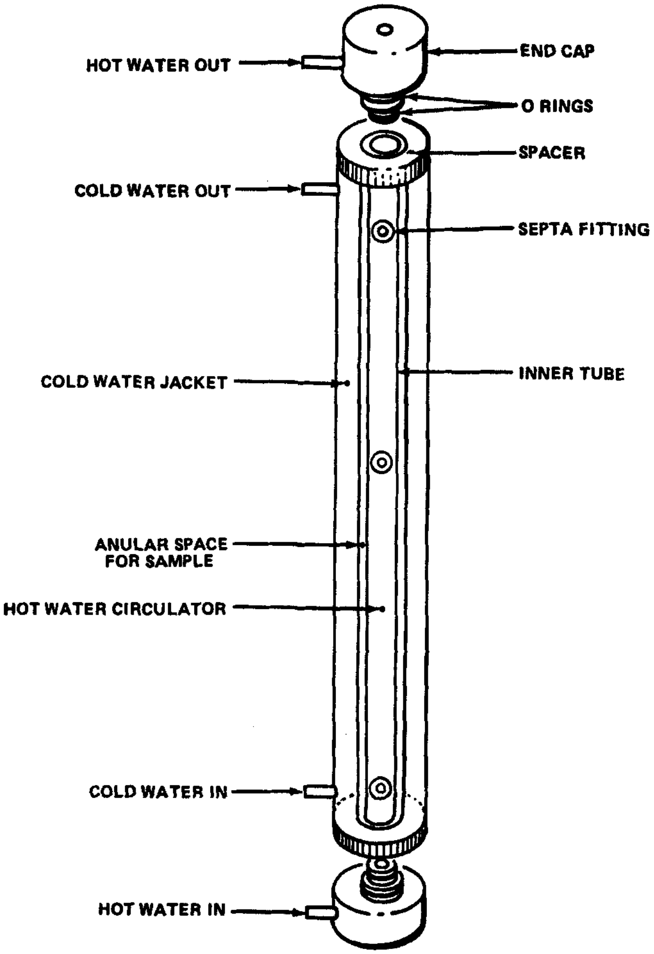


FIG. 25. Details of sample cell.

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 results emphasize the critical nature of the wall spacing and the need for further studies of wall spacing effects on separation.

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. The interesting result of these studies was that fairly rapid separation of aqueous copper sulfate solutions (0.13 *M*) was noted at large wall spacings (0.1 to 0.7 cm). Glass wool appeared to effect the most rapid separations. In one case the separation occurred in about 2 hr. As discussed in another section, the noted rapid separations in packed columns 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. As mentioned 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. The apparatus used in this portion of the study was especially constructed and consisted of two concentric brass cylinders. The cylinder walls were heated or cooled by water circulated along the cylinder walls. The brass cylinders were 25.4 cm long and the fluid column between them 20.32 cm long. The gap width between the cylinders was varied by slipping cylinders with different outer diameters over the inner cylinder. The following gap widths were used: 0.254, 0.127, and 0.0508 cm. The temperature difference was 20°C in most of the experiments. The apparatus was mounted on a circular Bakelite plate. This plate, in turn, was mounted on a circular aluminum plate turntable. The rotation rates utilized correspond to accelerations in the range of 10^{-4} to 10^{-3} g_g. The test fluid was an ethanol–water solution of 50% weight concentration. Concentrations were determined by measuring the refractive index of the solutions. The refractive index was measured with an ABBE-3L refractometer manufactured by Bausch and Lomb. Separation was determined by subtracting the ethanol concentration at the bottom from that at the top. At 0.0508 cm, separation was in the 0.15 to 0.20 range after 3 days of operation. Measurements were made with both a negative temperature gradient in the gap (a warm inner and a cold outer cylinder) and a positive temperature gradient (outer cylinder warm, inner cylinder cold) across the gap. In the first case a slight increase of separation with rotation rate was noted and a slight decrease in the second case. 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_g has, indeed, an effect on the separation in a rotating laterally heated annulus. Further studies, however, are indicated before a firm conclusion can be reached.

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 × 10.2 × 2.54 cm and 35.6 × 10.2 × 1 cm constructed with 1.91 cm thick Plexiglas 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 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 Plexiglas sides. The second technique used was an optical shadowgraph system.

Several experiments were run to determine if multicellular convection flows could be generated in the test cell. The preferred mode for a slab 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°C, and Ra $= 6 \times 10^6$, only the unicellular flow could be observed. Multicells were generated in inclined cells, however. Tests with packed cells were also conducted. The results of these studies unfortunately were inconclusive. Further studies in which temperature difference and cell wall spacing are further varied are indicated.

Potential Applications

Earth Applications. As mentioned previously, 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. It is felt that when adequately explored, the technique will undoubtedly find numerous applications in the biological separations area. The rather startling fast separation 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 perhaps 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., $T_H \sim 100°C$, $T_C \sim 30°C$.

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:

(a) Fractionation or purification of various oils with heat from generating plants or nuclear reaction plants.
(b) Conducting various polymerization reactions in conjunction with CD and waste heat.

Finally, CD might offer a potential as an energy conversion and storage device. Consider the situation depicted in Fig. 26. A 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

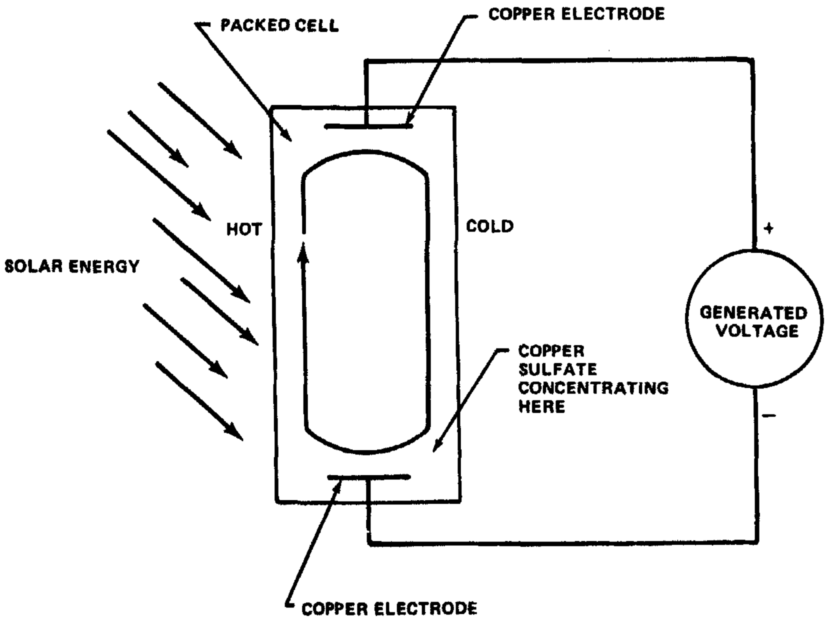


FIG. 26. An electrolytic CD solar concentration cell.

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 nonconvective "thermocells" (*110*). 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 μV/°C. The maximum efficiency is reported as 6.16%, comparable to 10% for the best thermoelectric generators currently used (*111*). 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.

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

(a) 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.

(b) Separation of certain specialty isotopes, ^{36}S from ^{32}S 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 Fig. 27.

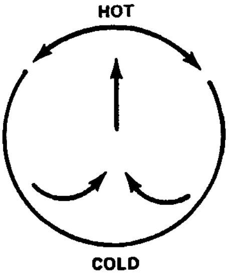


FIG. 27. Space CD of a floating molten sphere.

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 (*112–115*). 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.

Indicated Further Studies

The suggested earth 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 FFF, electrophoresis, adsorption, and chemical reactions, is also indicated.

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. Second, 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.

SYMBOLS

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 $\alpha\Delta T/2\bar{T}$.

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*
D'	liquid thermal diffusion coefficient, cm^2/sec-°C.* Positive if lighter solution component concentrates in warmer regions, negative if in colder regions. For heavier solution component, positive if concentration is in colder region and negative if in hotter region
D_T	gaseous thermal diffusion coefficient, cm^2/sec*
D_c	mole fraction diffusion coefficient*
D_w	weight fraction diffusion coefficient*
D_m	molar concentration diffusion coefficient*
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 $q_e = e^{HL/K}$, g/sec
J	mass flux, g/cm^2-sec
k	thermal diffusivity, cm^2/sec
k_T	thermal diffusion ratio, dimensionless
K	transport coefficient in equation $q_e = e^{HL/K}$. Also $K = K_c + K_d$, g-cm/sec
K_c	remixing transport coefficient, g-cm/sec
K_d	cell back diffusion transport coefficient, g-cm/sec
$\mathscr{L}$	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, g
$\overline{M}$	average molecular weight, g
n	number of moles
Nu	Nusselt number, heat transported/heat transported if conduction were the only means of heat transfer
P	pressure
Pr	Prandtl number $= \nu/k$, dimensionless

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*See note at end of listing.

q	separation factor at time t $\left(=\dfrac{c_e(1-c_s)}{c_s(1-c_e)}=\dfrac{w_e(1-w_s)}{w_s(1-w_e)}\right)$
q_e	separation factor at steady state
r_1	radius of outer cylindrical column
r_2	radius of inner cylindrical column
Ra	Rayleigh number $= g\beta\Delta Td^3/\nu k$, dimensionless
Re	Reynolds number $= \rho vL/\mu$, dimensionless
R	molar gas constant, 1.9872 cal/mole-°K
S_o	limiting entropy efficiency
SW	separative work
t	time
t_r'	time to reach $1/e$th of the steady-state separation factor q_e
T	temperature, °K
T'	a temperature different from T
T_H	temperature of the hot wall
T_C	temperature of the cold wall
ΔT	$T_H - T_C$, °C or °K
$\bar{T}$	mean temperature, $(T_H + T_C)/2$
USW	unit separative work
v	velocity, cm/sec
V	volume, cm^3
w	weight fraction and also $d/2$
W	one-half amount of feedstock or watts

Greek

α	thermal diffusion factor
β	coefficient of thermal expansion, $\dfrac{1}{V}\left(\dfrac{\partial V}{\partial T}\right)_P$, $-\dfrac{1}{\rho}\left(\dfrac{\partial \rho}{\partial T}\right)_P$, $(°\mathrm{K})^{-1}$
Δ	difference $c_e - c_s$
η	stage number
λ	thermal conductivity, cal/cm^2 sec°C/cm
μ	coefficient of viscosity, poise or g/cm-sec
ξ_e	experimental efficiency
ξ_o	limiting energy conversion efficiency
ρ	density, g/cm^3
σ	flow rate, g/sec; or Soret coefficient $(°\mathrm{C})^{-1}$
τ	rate of transport of a species, g/sec
ν	kinematic viscosity, cm^2/sec
χ	mass of gas per unit length of cell, g/cm
Ω	rotation rate

Subscripts

opt	optimum
1, 2	species designation or stage number
e	enriching end
s	stripping end
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. It might also be worth-while to mention that a confusion can also arise regarding values of diffusion coefficient when one set of concentration units is not used consistently. For example, it can be readily shown that:

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

$$D_c = \frac{m}{nc} D_m\left[2 - \frac{\partial \ln w}{\partial \ln c} + \frac{\partial \ln \rho}{\partial \ln c}\right]$$

Similar considerations apply to the value of the Soret coefficient σ. Because molarity changes with temperature, even though no mass has been added or subtracted, it is preferable to use only weight or mole fraction units consistently. (See Tyrrell reference given in the bibliography.) Weight fraction units appear preferable from the viewpoint of minimizing the potential for mistakes.

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