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The Porous Phase Barrier and Crystallization

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Abstract

A porous body can be used as a phase barrier, or to safely store or transmit a metastable fluid phase (B) under certain definable conditions even when a stable phase (A) outside the porous body is in intimate contact with the metastable phase inside the body. The condition to be met can be expressed by

$$R < 2\sigma V_A[(S_B - S_A)\cos\theta_A\,\delta T]$$

where R is effective ("cylindrical") radius of the pores; δT is degrees of supercooling (or superheating); σ is specific surface free energy of the phase boundary; θ_A is the contact angle of Phase A with the material of the porous body; V and S are partial molal volume and entropy of the indicated phases, respectively. Phase B, the "metastable" phase by conventional test, is found to be the stable phase so long as it remains confined within sufficiently small pores. If the "metastable" phase (B) is a supercooled liquid, strongly adsorbed by the porous material ($\theta_A > 90°$), Phase A can be crystalline, as demonstrated by the natural process of frost heaving of soil. This implies new methods of managing crystallization processes, including one whereby saline water is purified by an "ice sandwich" that sustains reverse osmosis and another whereby components of a binary eutectic mixture may be completely separated.

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A porous phase barrier can provide an additional degree of freedom in the management of crystallization processes by restraining the normal trend toward equilibrium. It is not known how many crystallization processes are subject to such manipulation but the list begins with water and evidently includes benzene and nitrobenzene. Investigation may reveal that the list is long. Likely candidates are substances whose melts strongly wet materials suitable for fabricating porous phase barriers, or which dissolve in liquids that can be so adsorbed.

The phase barrier principle is old and appears in an early exercise in elementary textbooks on thermodynamics, e.g., Lewis and Randall (*1*). The object of that exercise was to obtain a generalized form of the Clapeyron equation (attributed to H. LeChâtelier, 1892) for equilibrium involving systems of one component and two phases (*A* and *B*) under different pressures with the temperature (of the whole system) variable. In differential form this equation (their Eq. 14–7) is written:

$$V_B\, dP_B - V_A\, dP_A \doteq (S_B - S_A)dT = \frac{\Delta H}{T}\, dT \tag{1}$$

where V and S are the partial molal volumes and entropy, respectively, of water in the indicated phases; P is the pressure; T the (absolute) temperature; and ΔH the molar enthalpy of the phase transition.

To express Eq. (1) in finite form, we may start from a reference state in which Phases A and B are in normal equilibrium (at equal pressures) at temperature T. If the pressures of the respective phases are perturbed by finite (but unequal) amounts δP_A and δP_B, the temperature of both phases will, in general, have to be perturbed by some amount δT if the two phases are to continue to exist in mutual equilibrium. If δP_A, δP_B and δT are not too large, we may write

$$V_B\, \delta P_B - V_A\, \delta P_A = (S_B - S_A)\delta T \tag{2}$$

Hereafter, a special convention useful for this paper will be observed, namely $\delta P_A > \delta P_B \geqq 0$, with the reference state chosen to be consistent with this convention. The phase that is at the higher pressure will be always designated as *Phase A*, while the phase at a lower pressure will always be designated *Phase B*.

Equilibrium between two phases at unequal pressures can be established if they are placed on opposite sides of a suitable porous wall, a *phase barrier*, so named because it must have the property of preventing the high pressure phase, A, from penetrating its pores and passing into the space reserved for the low pressure phase, B, see Fig. 1. In the textbook example,

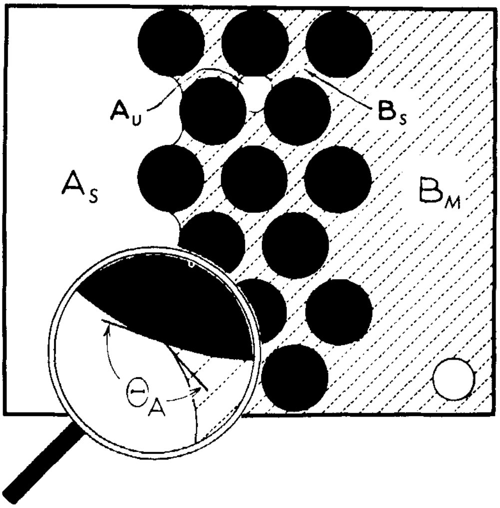

FIG. 1. Schematic diagram of two phases, A and B, held at unequal pressures by a porous phase barrier. In large spaces, the phase at higher pressure will be stable (A_s); the phase at lower pressure will be metastable (B_m). Within small enough pores, the situation is reversed with the higher pressure phase unstable (A_u) while the lower pressure phase will be stable (B_s). The enlarged feature shows the contact angle, θ_A, between the high pressure phase, A, and the material of which the phase barrier is made.

the phase barrier is a wall of fine porous porcelain; Phase A is liquid mercury and Phase B is mercury vapor. Liquid mercury does not wet porcelain, and within certain limits the liquid phase will be excluded from the pores by capillary effects while the vapor phase can traverse the pores freely in either direction.

Lewis and Randall emphasize that two phases at unequal pressure are not in true equilibrium, but they proceed on the assumption that reversible transitions between them can occur. Implicit in their exercise is the fact, not explicitly stated, that when $\delta P_A > \delta P_B \geqq 0$, Phase A is inherently stable while Phase B is inherently metastable, i.e., supercooled or superheated in the conventional usage of these terms. We will see, however, that the conventional test of metastability, namely insertion of a test body of another phase, reveals that while Phase B is metastable when present in a sufficiently large space, it is perfectly stable within sufficiently small pores of a suitable phase barrier. Conversely, Phase A is stable by this test when outside the phase barrier, but is rendered unstable if injected into small pores of the phase barrier. Accordingly, we will be careful to use A to designate the phase which, by the conventional test, is stable when outside the phase barrier, while B designates the "supercooled" or "superheated" phase that is metastable when outside the phase barrier.

An alternate statement of the convention for distinguishing between A and B can be given in terms of the contact angle between Phase A and the material comprising the phase barrier. This angle will be designated θ_A, see Fig. 1. The condition $\delta P_A > \delta P_B \geqq 0$ can only occur if $90° < \theta_A \leqslant 180°$.

It is evident that, in our usage of δP_A and δP_B,

$$\delta P_A - \delta P_B = P_A - P_B = \Delta P \tag{3}$$

where ΔP is the magnitude of the pressure jump in crossing the interface from Phase B to A.

Where the phase interface is opposite a pore in the phase barrier, Phase A will bulge into the pore, satisfying the Laplace equation:

$$\Delta P = 2\sigma/\bar{r} \tag{4}$$

in which σ is the specific interfacial free energy or surface tension, and $\bar{r}$ is the mean radius of curvature of the convex surface, as illustrated in Fig. 1. This diagram also illustrates (lower right corner) the minimum size of a test body capable of initiating reversion of the metastable phase, B, to the stable form, in accordance with concepts used in the theory of homogeneous nucleation. That is, to induce phase change, the test body (or "embryo") must have a mean radius of curvature larger than $\bar{r}$ of the equilibrium interface at the phase barrier. Study of the diagram also indicates that whereas a test body could survive if inserted within sufficiently large cavities inside the phase barrier, the requisite surface curvature could not be achieved in (cylindrical) pores smaller than a certain critical radius, R_{cr}, where

$$R_{cr} = 2\sigma/[\Delta P(-\cos\theta_A)] \tag{5}$$

That is, in pores smaller than the critical size an inserted test body of whatever volume must spontaneously disappear because there is no configuration of its interface that will satisfy the required contact angle without making $\bar{r}$ too small to satisfy Eq. (4).

The quantity ΔP can be defined in terms of a degree of supercooling or superheating of Phase B. Starting from "normal equilibrium" with

Phases A and B at the same pressure at temperature T, one can perturb the system by δT, holding P_B constant. From Eq. (2), when $\delta P_B = 0$,

$$\delta P_A = -(S_B - S_A)\delta T/V_A \tag{6}$$

Since our convention requires δP_A to be positive, δT will be positive (superheating) when $S_B < S_A$ but will be negative (supercooling) when $S_B > S_A$. In the textbook example, the molar entropy of mercury vapor (B) exceeds that of liquid mercury (A), so that δT is negative and gives the degrees of supercooling of the vapor phase.

If the phase barrier had been made of a sintered metal that was wetted by liquid mercury, the condition $90^\circ < \theta_A \leqslant 180^\circ$ means that Phase A would be the vapor phase and Phase B would be the liquid phase. According to the preceding paragraph, δT could only be positive, and would be the degrees of superheating of the liquid.

We may now combine Eqs. (3), (5) and (6) to obtain an alternate expression for the critical pore size in terms of δT, the degrees of supercooling or superheating of Phase B:

$$R_{cr} = 2\sigma V_A/[(S_B - S_A)\cos\theta_A \delta T] \tag{7}$$

To summarize, the voids of a suitable porous body can be used to safely store or to safely transmit a fluid, B, that is conventionally superheated or supercooled by an amount δT providing the pores are smaller than R_{cr} as given by Eq. (7).

PHASE BARRIERS AND CRYSTALLIZATION

Thus far the discussion constitutes straightforward exposition of facts implicit in Eq. (2) together with standard concepts of interfacial behavior in capillary systems where Phases A and B are both fluids. The main purpose of this paper, addressed to those who use crystallization processes as a means of separating components, is to call their attention to a nonintuitive fact; namely, that everything that has been said also applies when Phase A is a crystalline component and Phase B is its supercooled melt (or a supersaturated solution of the component) *if* the liquid phase strongly wets the material of which the phase barrier is made. This fact was discovered by those who study crystallization of water in soil and the attendant process of frost heaving.

Conceptual difficulties immediately arise when one attempts to visualize how pressure applied to a crystalline Phase A affects free energy content of the crystalline phase in close proximity to the phase barrier,

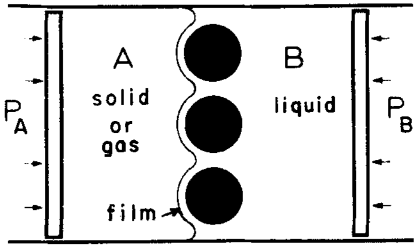

FIG. 2. Schematic diagram of a phase barrier strongly wetted by a liquid phase, *B*, that is in equilibrium with a solid or gaseous phase, *A*. In frost heaving, *A* would be ice at a pressure exceeding that of the pore water, *B*.

Fig. 2. One instinctively anticipates a complex stress pattern, with high pressure where the crystalline phase is pressed against the particles of the phase barrier, and lower pressure where it spans the opening of a pore with elastic energy stored in the strained crystalline phase. These difficulties, it turns out, vanish in the special case in which strong adsorption forces act on the liquid phase but not on the solid phase. It is helpful to review this special case since it is probably applicable to many systems, including the ice–water system.

It will be assumed that at every point on the interface (Fig. 2) there will be equilibrium between the liquid and solid phases. The interface is free to alter its shape through phase changes until all local shearing stresses in the crystalline phase are relieved, and the associated stored energy is dissipated, leaving only the simple condition of uniform pressure throughout the solid phase. In the liquid phase, however, pressure is *not* uniform. At equilibrium, liquid just inside the interface in the film has suffered a loss of free energy due to the adsorption phenomenon and this just offsets the free energy increase due to the local increase in pressure.

If this proposition has not been stated convincingly, perhaps the following analog will be more illuminating, again referring to Fig. 2. Consider a system in which Phase *A* is air at atmospheric pressure and Phase *B* is water at room temperature with a phase barrier of fine porcelain, or a filter paper, strongly wetted by water. Holding temperature and water pressure constant, raise the air pressure somewhat above atmospheric pressure (whereupon the liquid phase will soon become a metastable supersaturated solution of air). We expect the extremities of the porcelain, protruding into the air phase, to possess absorbed films of liquid water, since porcelain is somewhat hygroscopic. If we assume that the surface adsorption forces terminate, for all practical purposes, at the film–air interface (and we will mention a likely model of such forces), then the air, and water vapor in the air, do not experience these forces. Consequently, we expect the air phase to be isobaric throughout, since it cannot sustain shearing stresses when at rest and experiences no local body force fields. We conclude that there must be pressure fluctuations in the liquid phase beneath the undulating topography of the air–water interface, and explain them in a manner such as that attempted above. The free energy of the water is everywhere defined by the temperature and the pressure applied to the water in bulk, to the right of the phase barrier in Fig. 2.

If Phase *A* were ice, instead of air, and if the ice also experienced no body forces (adsorption forces) near the interface, its minimum free energy content would result when, by phase change, the interface attained a shape for which the ice became isobaric throughout, just as the air was isobaric. This condition would be reached if the topography of the interface acquired the same topography as the air–water interface, i.e., when, opposite the pores, $1/\bar{r}_{iw} = 1/\bar{r}_{aw}$ where *iw* signifies the ice–water interface and *aw* signifies the air–water interface. These curvatures will be the same when $(\Delta P_{iw}/\sigma_{iw}) = (\Delta P_{aw}/\sigma_{aw})$.

Accordingly, we conclude that the free energy of water in the ice phase is not only everywhere defined by temperature and pressure applied at a distance from the phase barrier, but also the convenience of assuming uniform ice pressure throughout is rational, despite initial instincts to the contrary.

The foregoing concepts of close correspondence between the geometry of air–water and ice–water interfaces have been verified for soil–water–air and soil–water–ice systems. These experiments yielded $\sigma_{aw}/\sigma_{iw} = 2.20$ for the ratio of the surface tensions of the respective interfaces over a substantial range of values of ΔP (*2*).

What is the nature of the adsorption mechanism? Many surface chemists concentrate their attention on phenomena involving adsorption of one or two monolayers from gases or vapors at low pressures, and they think in terms of chemisorption and van der Waals forces which can produce very strong adsorption forces for very short distances. Those who study adsorption from nearly saturated vapors, however, find other mechanisms to explain the adsorption of thick films, which may have thicknesses of tens or scores of molecular diameters, and involve long range forces. Prominent among the postulated mechanisms is one based on the Gouy-Chapman model of the diffuse electrical double layer, in which swarms of ions in solution selectively congregate near a surface that has a fixed lattice charge, or which has an effective charge owing to preferential attachment of ions of one sign to the surface (*3*). The net charge of the diffuse ion swarm must balance the net charge of the surface. The ions are effectively in solution, but are mostly of one sign and are constrained to be distributed laterally over the surface in close correspondence to the distribution of charge on the surface of the particle. If the liquid phase is attenuated by evaporation, the counterion concentration of the residual film increases, lowering the vapor pressure of the film. If, as in our example, the film were "compressed" by the air phase, water would be squeezed laterally from the films into the pore system until the osmotic pressure of the residual film, with its counterion content, became sufficient to prevent further loss of water to the bulk water to the right of the phase barrier. In this model the "adsorption forces" act only if the ions of the diffuse double layer are present. That is, the adsorption forces would act only *within* the liquid phase, and would terminate at the air–water interface. The same model has been postulated when the nonliquid phase is ice instead of air (*4*). Partition by crystallization excludes ions from the ice side of the interface, corresponding to exclusion of ions from the air phase; as the ice phase encroaches on the double-layer region the freezing point of the residual "solution" would be depressed and the osmotic pressure would rise.

Even if there is some uncertainty as to the relative importance of the double-layer mechanism and other postulated mechanisms for unfrozen films, students of the phenomenon of frost heaving in soils conclude, in effect, that reversible transitions between massive ice and "supercooled" (but stable) pore water occur when soil freezes or thaws in accordance with the phase barrier concepts described above, with ice being Phase *A* (*4–9*). The experiments of Taber, Fig. 3, led him to postulate the existence and functions of the adsorbed films (*10*).

Frost heaving, as demonstrated by Taber, is the growth of lenticular bodies of pure ice in soil that is being frozen from the top downward; the as yet unfrozen soil supplies or conducts water to the base of a growing lens. As the ice lens thickens, very great loads (tons per square foot) may be lifted, making frost heaving a very destructive natural force that can be attributed to a phase barrier effect. Taber reported that heaving could be produced in soils wetted with benzene or nitrobenzene instead of water. He used these liquids, which contract on freezing, to disprove

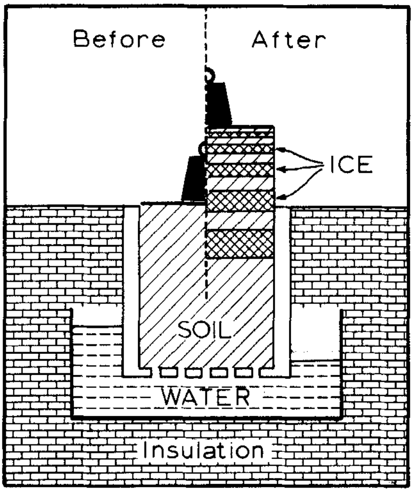

FIG. 3. Schematic representation of Taber's classic frost heaving experiment (*13*), before and after exposure of the surface of a column of wet soil (which bore a load) to subfreezing temperatures. The load was lifted by the sequential growth of a series of ice lenses whose aggregate thickness equaled the total uplift. The basal reservoir lost water equivalent to the volume of ice in the lenses. When benzene or nitrobenzene was used instead of water to wet the column and to fill the basal reservoir, similar results were obtained.

once and for all the common (and still prevalent) presumption that frost heaving is due to the expansion of water when it freezes.

Lenticular single crystals of gypsum that evidently pushed back the soil as they grew have been found in the barren sabkhas along the Persian Gulf where saline ground water, ocean water, and evaporation combine to produce a saturated (or supersaturated) solution (*11*). Thus it appears that frost heaving has at least one natural analog involving a crystalline solid and a solution phase. Doubtless there are many more if we know what to look for; perhaps some geodes form in this way. Everett, whose treatment of the surface tension effect in heaving was definitive (*5*), has suggested that destruction of porous building materials may be traced to growth of ice or mineral crystals within cavities that are effectively surrounded by a porous phase barrier that contains a mother liquor that nurtures crystal growth in the cavity but at the same time physically restrains growth until fracture occurs.

Given these indications that phase barriers can be operative in certain solid–liquid transitions, it is tempting to speculate on diverse roles for phase barriers in the management of crystallization processes where separation of components is the objective.

The author has briefly described elsewhere (*12*, *13*) an example of a purification process using a device called the *ice sandwich*, Fig. 4. In this device a thin body of ice fully occupied the space between two parallel filters that served as phase barriers. Outside one barrier, a saline solution was circulated at pressure p_l (gauge). Outside the other barrier was pure water at atmospheric pressure. The assembly was immersed in a bath at temperature t°C, where t was slightly below the freezing temperature of the solution, i.e., both liquid phases were supercooled. When p_l was equal to the osmotic pressure, Π, of the solution, nothing happened (Fig. 5). When p_l was less than Π, water appeared in the solution and disappeared from the other side, simulating osmosis. When p_l exceeded Π, water disappeared from the solution and appeared on the other side, simulating reverse osmosis, and served as a means of separating pure water from a solution.

To analyze the expected performance of the ice sandwich, Eq. (2) may be further extended to include the effects of solutes. Since ice and pure pure water ($\Pi = 0$), both at atmospheric pressure ($p_l = p_s = 0$, gauge pressure), are at equilibrium at $t \equiv 0$°C, the equation may be rewritten for other temperatures, pressures and solution concentrations:

$$\bar{V}_l(P_l - \Pi')_l - \bar{V}_s p_s = (S_l - S_s)t \tag{8}$$

In this equation, V and S are partial molal volume and entropy of water

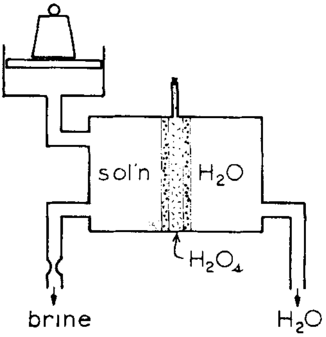

FIG. 4. Schematic diagram of prototype ice sandwich for purification of water by reverse osmosis. Solution in input chamber (left) and water in output chamber (right) are both supercooled.

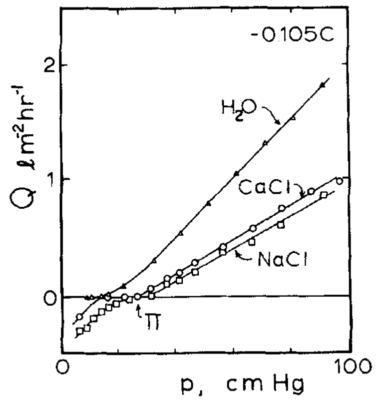

FIG. 5. Water movement through prototype ice sandwich with water or aqueous solutions on one side at pressure p (gauge) and water at atmospheric pressure on the other side. Negative flow simulates osmosis; positive flow simulates reverse osmosis. The calculated osmotic pressure of both solutions is indicated. Dead bands are attributed to friction of the ice at the periphery of the ice chamber.

in the indicated phases, respectively; subscirpts l and s signify liquid and ice phase, respectively; Π' is the osmotic pressure of the solution in contact with the interface; p is the gauge pressure of the indicated phase, and t is the temperature in degrees centigrade.

Transport of water across the ice sandwich involves two mechanisms in series; diffusion through a stagnant solution layer to the ice surface, and translational movement of the ice phase accomplished by concurrent freezing and melting at opposite sides of the ice layer. The rate of transport by ice is therefore limited by the rate of conduction of the heat of fusion to and from the respective surfaces.

From Eq. (8) we find that where ice at pressure p_s is in contact with solution,

$$t = [V_l(p_l - \Pi') - V_s p]/(S_l - S_s) \tag{9}$$

If pure water on the opposite side is at atmospheric pressure,

$$t = (-\bar{V}_s p_s)/(S_l - S_s) \tag{10}$$

If peripheral friction that restrains ice movement in the chamber is negligible, the ice pressure, p_s, must be uniform, hence the temperature gradient across the ice must be

$$(dt/dx)_s = V_l(p - \Pi')/[\tau_s(S_l - S_s)] \simeq V_l(p - \Pi')T/(\Delta H \tau_s) \quad (11)$$

where τ_s is the thickness of the ice layer. Observe that the ice pressure exceeds either liquid pressure, and the temperature gradient is in a direction such that heat flow across the ice will be in the same direction as the ice moves. Let τ_s be so small in comparison with heat paths leading to the constant temperature bath that heat flow will be almost entirely across the ice. In this circumstance, transport of water, Q, will correspond to heat transport, Q_h, across the ice. In the limit,

$$Q = Q_h/\lambda = (1/\lambda)k_s(dt/dx) \quad (12)$$

where λ is the latent heat of fusion and k_s is the thermal conductivity of ice.

If it is assumed that transport of water across the stagnant layer is accomplished by simple diffusion:

$$Q = \rho_l D[\ln(\Pi'/\Pi)]/\tau_l \quad (13)$$

where ρ_l is the water density in the solution, D is the diffusion coefficient, and τ_l is the effective thickness of the stagnant layer. If $\bar{V}_l/(S_l - S_s)$ is taken to be $(T/\rho_l\lambda)$, combining Eq. (11), (12), and (13) to eliminate Π' gives an expression relating pressure and concentration of solution in the input chamber to rate of production of pure water:

$$P_l = (Q\tau_s\lambda^2\rho_l/k_sT) + \Pi \exp(Q\tau_l/\rho_l D) \quad (14)$$

Figure 6 was obtained from Eq. (14) and shows that with brackish water, too saline for domestic use, but about one-fourth the concentration of seawater, the calculated rate of production would be much more sensitive to the thickness of the stagnant layer than to ice thickness. With more dilute solutions, the relative importance of stagnant layer thickness diminishes and predicted yields increase rapidly.

The stagnant layer is comprised of liquid in the pores of the phase barrier and a laminar flow region between the phase barrier and the turbulent flow region in the input chamber. The contribution of the phase barrier to stagnant layer thickness tends to impair the competitive position of the ice sandwich for reverse osmosis processes involving concentrated solutions. On the other hand, the potential for very high performance with dilute input solutions, coupled with the highly selective action of crystallization, suggests that the ice sandwich deserves consideration as an alternative to distillation or deionization for the production of extremely pure water for technical purposes. This capability is enhanced by the fact

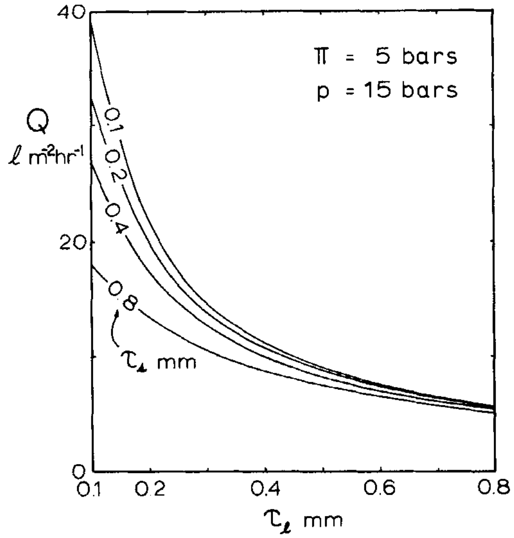

FIG. 6. An example of expected production of pure water from a saline solution by an ice sandwich as computed from Eq. (14) with indicated values of ice and stagnant layer thicknesses, τ_s and τ_l, respectively.

that successive stages of purification could be arranged in cascade in a single constant temperature bath giving, in effect, a multiple zone-melting process that is conveniently controlled by pressure regulation, rather than by heat regulation. If this were attempted and experience proved favorable, efforts to extend the range to more and more concentrated solutions through improved phase barrier design (*12*) would be called for. Meanwhile, the ice sandwich scheme might be used to advantage for purifying freezable solvents other than water.

Other novel applications of phase barriers come to mind (Fig. 7). For example, it may be possible to completely isolate the components of a binary solution of eutectic composition. If such a solution were fed into the edge of a porous sheet held at a temperature slightly below the eutectic temperature, seeding the respective sides with crystals of pure components should result in continuous formation of two crystalline components, isolated from each other by the intervening phase barrier. The phase barrier, of course, must be of a substance that is wetted by the liquid phase. If necessary, to suppress premature crystallization, the liquid could be supercooled after it is safely inside a porous duct leading to the edge of the phase barrier.

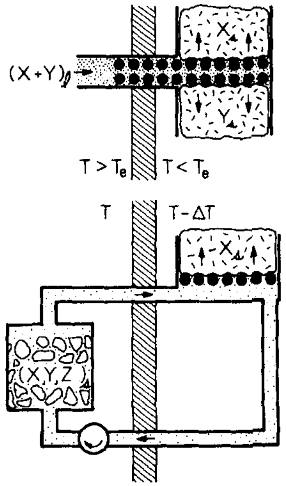

FIG. 7. Suggested applications of phase barriers in purification processes. *Top*: Scheme for separating components, X and Y, of a binary eutectic mixture with eutectic temperature, T_e. *Bottom*: Scheme for extracting a single component, X, from a mixture of soluble solids (X, Y, Z, . . .) using a recirculating solvent.

Another possible application would be selective extraction of one component from a mixture of soluble solids. To do this, the mixture could be leached by a solvent which would then be cooled slightly and passed beneath a phase barrier seeded with crystals of the component to be extracted. The solvent would then be rewarmed and recirculated. Eventually all of the desired component should be removed and recrystallized outside the phase barrier except for the residue dissolved in the circulating solution.

While stagnant layer impedance may impair the efficiency of purification processes using phase barriers, processes that could not be contemplated otherwise can be imagined using the control of crystallization that phase barriers provide when the liquid phase interacts suitably with the substance of the phase barrier. At this time, it appears that water, benzene, and nitrobenzene interact suitably with certain silicates, and water interacts suitably with cellulose, but no systematic exploration of the possible range of combinations has been attempted. The capacity of a porous phase barrier to safely deliver a fluid in a supercooled, superheated, or supersaturated state to a crystallization or reaction site may have applications other than those mentioned.

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