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Purification of Materials as a Branch of Science

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KEYNOTE ARTICLE

Purification of Materials as a Branch of Science*

It is truly wonderful to find assembled here a conference of experts—experts of the widest diversity of training and interest, yet having in common a concern for the purification and separation of materials. However, despite the existence of this very assembly, and despite the increasing number of symposia on the topic of purification, I feel that the scientific community, on the whole, has failed to recognize the importance of purification and separation of materials. I refer not only to the many researches wasted on materials whose impurities obscured the true properties and rendered the researches worthless—that is an old story—but I refer also to the need to recognize that the field of purification and separation of materials is a legitimate branch of science in its own right, a field worthy of the best that talented minds can bring to bear.

When I referred to purification as a branch of science, I did not intend to exclude engineering. It is sometimes difficult to tell where one ends and the other begins, and efforts in these two disciplines can and should be complementary. There is one difference between the two disciplines that is important, however. That is the matter of time. An engineer told to come up with a desalination plant in six months is unlikely to explore untried paths. Yet the kind of training and knowledge possessed by chemical engineers is essential to advances in purification and separation.

SOME COMMON FEATURES OF SEPARATION METHODS

To find some common features among the vast variety of interests represented here, it may be well to define what is being discussed.

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* Based on a paper presented at the Conference on "Purification of Materials," New York Academy of Sciences, New York, May 1965.

T. Melnechuk,[*] in an excellent general article on separation methods, used the system "fish afloat in salt water" as an illustration. He described this system as heterogeneous. Having more than one phase it could be separated by a mechanical device, a net. But the system "salt dissolved in water" is homogeneous. Having only one phase, it cannot be separated into its components mechanically. It requires some change in its physical chemistry. Although these remarks are to some extent an oversimplification, they can nevertheless be used to define the kind of system I wish to discuss, namely, the homogeneous.

Given such a homogeneous system, comprised of two or more components, the act of separation requires first of all that a concentration difference be established between two *regions* of the system. Shortly we shall examine the methods that have been used to produce such a concentration difference. But first, let us again divide systems into two classes for discussion. This can be done on the basis of the *magnitude* of the concentration difference.

If the separation is perfect, or for practical purposes, nearly so, all of a desired component will be present in one of these two regions, and all of the other component or components will be present in the other region. There are processes that do just this. Certain clathrate compounds are very specific in their behavior. The freezing of sea water is another example. One freezing, properly performed, could provide water pure enough to drink (if only we knew how to perform it properly). Thus, there is a class of systems for which one separation step, *properly performed,* could achieve the desired separation. The main problem to be faced in considering separations for systems of this class is how best to perform the single separation step required.

However, most of the systems with which this conference is concerned involve concentration differences of small magnitude. Such systems require, therefore, in addition to the establishment of this small concentration difference, the *countercurrent* flow of regions of the system between which these small concentration differences exist. Such countercurrent flow, with repeated equilibrations of opposed regions, multiplies the original small concentration differences—adding them end to end, so to speak—so that, over-all, a large separation is achieved. There are many ways

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[*] T. Melnechuk, *International Science and Technology*, p. 23, February 1963.

of producing these countercurrent flows: some obvious, some clumsy, some so subtle as to be scarcely detectable. An important problem for the science of separations is to discover, and delineate, and analyze the variety of countercurrent flow processes that can be utilized against Nature to achieve desired separations.

Having mentioned Nature, let us face the fact. Separation is against Nature. Cottrell,[*] in a text on physical metallurgy, nicely brought out the way in which entropy opposes the production of a perfectly pure crystal. The increase in the configurational entropy, or the entropy of mixing, is very great indeed, as very small concentrations of impurity are added to a pure crystal. This is shown in Fig. 1. Since thermodynamics tells us that an increase in entropy decreases free energy, thermodynamics seems to be against purification of materials.

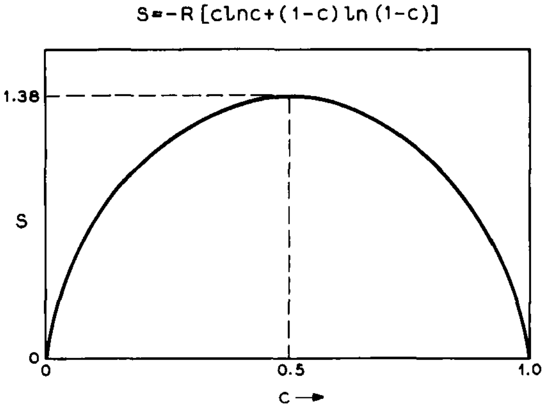

FIG. 1. Configurational entropy, S, of a crystal as a function of atom fraction, c, of impurity.

An important adjunct to the concept of countercurrent flows is the concept of *reflux*. Introduced in connection with distillation, it has somewhat vaguely emerged as a concept that should stand on its own and be applicable to other separation methods. By reflux is meant the return, at the end of the apparatus, of the material of the arriving stream to the leaving stream. Practically, reflux has proved to be useful mainly for concentration differences produced by a change of phase, as in distillation, or zone

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[*] A. H. Cottrell, *Theoretical Structural Metallurgy*, Arnold, London, 1948, p. 110.

melting. It has been described by some writers as very subtle, and difficult to understand, and to an extent I agree. However, if you will take the trouble to play a game of squares and numbers with countercurrent flow, involving say five stages of separation, and a fixed equilibrium concentration ratio between adjacent squares, say 2:1, you will quickly discover the difference between two countercurrent streams feeding in fixed compositions and leaving at the opposite ends, and two circulating streams (representing total reflux), in which the exiting composition of stream *A* is returned to the circuit as the entering composition of stream *B*.

I have talked for some time about these concentration differences in our system. We should consider how they are to be produced.

METHODS OF PRODUCING CONCENTRATION DIFFERENCES

Change of phase is one of the most common and was one of the earliest to be used. If we consider that there are three phases—solid, liquid, and vapor (ignoring the plasma phase of matter)—there are six phase changes that conceivably could be used: (1) solid-solid, (2) solid-liquid, (3) solid-vapor, (4) liquid-liquid, (5) liquid-vapor, and (6) vapor-vapor.

The two most used are solid-liquid and liquid-vapor. It is significant that it is only in recent years that both of these centuries-old transformations have been made truly effective by the introduction of new techniques of countercurrent flow.

To illustrate, let us consider multiple-crystallizations. There are well-known "triangular" and "pyramid" schemes for separating and recombining crystals and mother liquors. These are troublesome and time-consuming. Yet, in a related method, distillation, we now have rather efficient and easy-to-operate distillation columns, with countercurrent flows of liquid and vapor. It was surprising to me to learn that such distillation columns are of relatively recent origin, and that up to then the same type of inefficient operation as mentioned above for repeated crystallizations had been used.

One wonders why the analogy has not been used in reverse. The answer is that it has been tried. The column crystallizers developed recently by Professor Schildknecht* and co-workers

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* H. Schildknecht, Normal freezing, zone-melting, and column crystallization, *Z. Anal. Chem.*, **181**, 254 (1961).

and some of the precursors of these devices) all attempt to build a crystallizer exactly modeled after a distillation column, with countercurrent flows and reflux. The main problem is that crystals do not rise as readily as vapor does, and mechanical means are needed.

Yet, in zone refining, the desired simplification of multistage crystallization has been realized in a way not at all obvious when thinking by analogy. A batch-zone refiner in the steady state is quite like a still operated at total reflux. Even though in a zone refiner countercurrent flows of solid and liquid do not actually occur, the effect of passing molten zones along the refiner is just the same as if countercurrent flows and equilibration of solid with liquid had occurred.

There is every reason to believe that other such breakthroughs remain to be found. The search for such new approaches to countercurrent flow should be another aim of the science of separation methods.

Phase changes are a desirable way to produce concentration differences because they require no foreign substance. Another closely related technique involves surface-active solutes, that is, components of a solution that prefer to remain on the surface. Exploitation of this phenomenon by the technique of foam separation has usually, however, involved introducing a foreign substance that enhanced the surface preference of a particular solute, and hence has added complexity to the separation.

Another partition technique involves two separate immiscible liquids, for example, liquid-liquid extraction. Countercurrent flows have been achieved by various ingenious means. Because two different substances are involved, reflux has usually proved impractical.

Another, and major, class of methods of producing the small concentration differences later to be multiplied by countercurrent flow and possibly reflux may be called *kinetic*. In all these methods the system is subjected to a field of some sort. The field causes the components to travel, with respect to one another, or with respect to a medium in which they are contained. Differing rates of travel enable a separation to be made. What are some of these fields, or gradients?

1. Compositional (diffusional separations).
2. Electrical (electrophoresis, electrodiffusion, electrodialysis, field freezing).

3. Gravitational (centrifuging).
4. Thermal (thermal diffusion).
5. Magnetic-electrostatic (mass spectrographic).

In most of the methods of this class, the compositional difference is small, and a premium is placed on effective countercurrent procedures.

ENERGY REQUIREMENTS

Thermodynamics, of course, places an irreducible minimum on the energy required for a given separation. In practice, the energy required is usually much greater than this minimum.

On a commercial scale, time, energy, and holdup are significant. On a research, or laboratory scale, energy is less important, but time is significant. In this area, engineering and science meet. At one end is how to do the job most cheaply. At the other is how to do it at all. Advances in the sciences are predicated on the latter. Converting these advances to common use is predicated on the former.

To sum up, advances in the field of separation and purification have been retarded, in my opinion, because of the lack of a feeling of commonality on the part of the diverse disciplines involved. There is much common ground for a science of purification. Major goals of such a science, both in theory and in practice, can be: (1) to learn how to perform single-stage separations more effectively, (2) to seek new methods of producing concentration differences in a system, (3) to seek new methods of utilizing countercurrent flow and reflux, (4) to seek out and define the underlying unity of the various classes of materials and methods involved, and (5) to express this underlying unity in basic, elementary theoretical form, much as thermodynamics underlies the various sciences today. We need a Willard Gibbs for separation processes.

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