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A TWO LIQUID PHASE DISTRIBUTION METHOD FOR THE  
SEPARATION OF METALLIC ELEMENTS\*

by

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ABSTRACT

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The general principles of a liquid-liquid solvent extraction method for the separation of metallic elements are outlined.

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\* Manhattan Project Report CN-2486, December 19, 1944.

\*\* The work described in this paper was sponsored by the Atomic Energy Commission.

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A TWO LIQUID PHASE DISTRIBUTION METHOD FOR THE  
SEPARATION OF METALLIC ELEMENTS\*

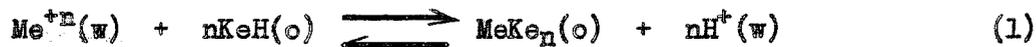
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In view of recent publications (1,2,3) describing the separation of certain elements by solvent distribution methods involving chelation it seems desirable to record the general principles of such a method which were evolved some years ago. The method depends upon the formation of un-ionized chelate compounds by the elements with certain organic reagents and the small solubility of these compounds in water compared to their solubility in water-immiscible organic solvents. The overall equilibrium involved in the transfer of the element between the aqueous phase and the organic phase may be represented by the following equation (1):



where  $\text{Me}^{+n}$  represents the metal ion of oxidation number  $n$ ;  $\text{KeH}$  represents the organic chelating group;  $\text{MeK}_n$  represents the metal chelate;  $(\text{w})$  represents the water phase; and  $(\text{o})$  represents the organic phase.

\* Manhattan Project Report CN-2486, December 19, 1944.

\*\* The work described in this paper was sponsored by the Atomic Energy Commission.

- (1) E. Aprahameczik, *Angew. Chemie*, 61, 98 (1949).
- (2) H. Gotte, *Z. Naturforsch.*, 1, 377 (1946).
- (3) B. G. Harvey, H. G. Heal, A. G. Maddock and E. I. Rowley, *J. Chem. Soc. (London)*, 1947, 1010.

One may define an equilibrium constant,  $K_{Me}$ , for a given element, Me, with a particular organic system as follows:

$$K = \frac{[MeK_n(o)] [H^+(w)]}{[Me^{+n}(w)] [KeH(o)]} = D_{Me\left(\frac{o}{w}\right)} \frac{[H^+(w)]^n}{[KeH(o)]^n} \quad (2)$$

where  $D_{Me\left(\frac{o}{w}\right)}$  represents the distribution ratio for the element expressed as the total concentration of the element in the organic phase divided by the total concentration of the element in the water phase.

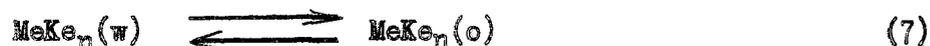
Thus, for any given element, Me, with a particular organic system, the distribution coefficient is given by equation (3):

$$D_{Me\left(\frac{o}{w}\right)} = K_{Me} \frac{[KeH(o)]^n}{[H^+(w)]^n} \quad (3)$$

Since the value of  $K_{Me}$  is different for each element (4,5,6,7,8) it is clear how such a system may be used for the separation of the elements.

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- (4) M. Calvin and K. Wilson, J. Am. Chem. Soc., 67, 2003 (1945).  
 (5) M. Calvin and R. H. Bailes, J. Am. Chem. Soc., 68, 949 (1946).  
 (6) R. B. Duffield and M. Calvin, J. Am. Chem. Soc., 68, 557 (1946).  
 (7) M. Calvin and N. C. Melchior, J. Am. Chem. Soc., 70, 3270 (1948).  
 (8) M. Calvin and N. C. Melchior, J. Am. Chem. Soc., 70, 3273 (1948).
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It should be pointed out that equation (1) is only an approximation and represents the resultant of several independent equilibria. An examination of these equilibria will reveal the various factors which determine the design and choice of the chelating agent, represented by KeH. The equilibrium (1) thus consists of the sum of the four following equilibria:



It is clear that some of the desirable properties in KeH, that is, properties which would lead to a high distribution constant in favor of the organic phase, tend to be mutually exclusive. For example, the relative solubility of the metal chelate in the organic phase should be high, whereas the relative solubility of the chelating agent in the organic phase would better be lower so as to increase the amount of chelating ion in the water phase. It is to be expected that these two desiderata will be effected in opposite directions by structural changes in KeH.

Perhaps one of the most important characteristics of the chelating agent is its acid dissociation constant. While it is true that, in general, the chelation constant representing the stability of the metal chelate compound (equation 6) varies inversely with the acid strength, there are factors determining the chelate stability independent of those factors determining acid strength (4,5,6,7,8). It is thus possible to select a chelating agent

having a fairly high acid dissociation constant so as to produce fairly high concentrations of the chelating ion in the water phase,  $Ke^-(w)$ , without losing the intrinsic ability of the agent to form a chelate compound.

The particular group of compounds which have been most successful are represented by the beta-diketones of the structure (9)  $X-\overset{\text{O}}{\parallel}{C}-CH_2-\overset{\text{O}}{\parallel}{C}-CF_3$ , the  $CF_3$  group being introduced to increase the acidity of the enol form without destroying the resonance in the metal chelate compound. A very useful organic solvent is benzene.

The method of operation is relatively simple. The elements may be arranged in the order of the value of their equilibrium constants,  $K$  (equations 2 and 3). In order to isolate any particular element from such a mixture it is necessary only to adjust the hydrogen ion concentration and the chelating group concentration such that all the elements having values of the constant larger than the desired element plus the desired element are removed from the water phase into the organic phase. This is then followed by a re-extraction of the organic phase by a water phase having a somewhat higher acid concentration such that the desired element is the only one re-extracted into the water phase since it must, of necessity, have the lowest value of  $K$  of all the elements in the organic phase.

If the  $K$  values are sufficiently widely separated in any particular mixture, substantial purity of the element can be obtained in a single cycle, that is, once into the organic phase and once returned to the aqueous phase. However, if the values of  $K$  are too close together to allow such a separation in a single cycle, it is quite clear how a multiple cycle arrangement may be

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(9) J. C. Reid and M. Calvin, J. Am. Chem. Soc., in press.

achieved and a fractionation of the elements accomplished in much the same way as a fractional distillation is accomplished except that in this case the two phases are both liquid.