développante (N), la détermination de la développante (P) se ramène à l'étude de l'équation de RICCATI(1). On n'a donc pas une seule courbe (P) mais toute une famille de courbes projectivement égales parce que dépendant homographiquement d'une même constante d'intégration.

Si maintenant nous envisageons le cas particulier $\chi(t) = -\sigma_1(t)$, c 'est-à-dire celui où la développante généralisée (P) se réduit à une développante classique de la courbe (N), l'équation (1) se ramène à la forme

$$B\,\sigma_1'' - \sigma_1\,(B' + \sigma_1'^2) = 0, \tag{3}$$

équation différentielle du second ordre en $\tau(t)$ qui fournit la développante (N) associée à la courbe-base (M). Comme autre cas particulier, signalons celui pour lequel la normale en N à la courbe (N) passe par le point L. Reprenant les relations (2), la condition $B = 0$ s'écrit

$$\tau' + \sigma' = \frac{\omega_1\,\alpha'\,\tau}{\omega_2 - \sigma'\,\tau}. \tag{4}$$

Nous utilisons la notation

$$\lambda^2 = \omega_1^2 + (\omega_2 - \sigma'\,\tau)^2 \text{ soit } \overline{NL}^2 = \left(\frac{\lambda}{\sigma'}\right)^2. \tag{5}$$

La développante (P) est alors déterminée par l'équation de RICCATI réduite

$$\chi' - \frac{\beta'}{\lambda}\,\chi^2 + \sigma_1' = 0, \tag{6}$$

équation que nous avons déjà rencontrée dans une précédente étude.

Il est intéressant de la rapprocher de la forme réduite de M. ELIE CARTAN[1]

$$\chi' + P\,\chi^2 + 1 = 0. \tag{7}$$

Nous avons

$$\sigma_1' = 1,\ P = -\frac{\sigma_1'}{\varrho_1\,\lambda},\ \varrho_1 = \frac{\sigma_1'}{\beta'}. \tag{8}$$

Ainsi pour deux développantes (N) à paramétrisation isométrique, nous obtenons, entre les distances $\overline{NL}$ et $\overline{N^*L^*}$ correspondantes la relation

$$\frac{\overline{NL}}{\overline{N^*L^*}} = \frac{\varrho_1^*}{\varrho_1} \cdot \frac{\sigma'^*}{\sigma'};\ (\sigma_1' = \sigma_1'^* = 1). \tag{9}$$

GABRIEL VIGUIER

Institut H. Poincaré, Paris, le 30 septembre 1949.

Summary

From an absolutely arbitrary plane curve, particular involutes are drawn the study of which is reduced to that of a differential equation of the second order. As a particular case, ABEL's equation is derived again, also RICCATI's equation with the reduced form of E. CARTAN.

[1] E. CARTAN, *Théorie des espaces a connexion projective* (Gauthier Villars, Paris 1937).

A Two-Liquid Phase Distribution Method for the Separation of Metallic Elements[1]

In view of recent publications[2] 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 unionized 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[3]. 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[4]:

$$Me^{+n}(w) + nKeH(o) \rightleftharpoons MeKe_n(o) + nH^+(w) \tag{1}$$

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

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

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

where $D_{Me}\left(\frac{o}{w}\right)$ represents the distribution ration 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:

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

Since the value of K_{Me} is different for each element[5] it is clear how such a system may be used for the separation of the elements.

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:

[1] Manhattan Project Report CN-2186, December 19, 1944.

[2] E. ABRAHAMCZIK, Angew. Chemie *61*, 98 (1949). – H. GÖRTE, Z. Naturforsch. *1*, 377 (1946). – B. G. HARVEY, G. HEAL, A. G. MADDOCK, and E. I. ROWLEY, J. Chem. Soc. *1947*, 1010 (London).

[3] Solvent extraction methods with or without complexing agents have been in use in an empirical way in analytical chemistry for some time. See WICHMAN, Ind. Eng. Chem. Anal. Ed. *11*, 66 (1939) and T. MOELLER, Ind. Eng. Chem. Anal. Ed. *15*, 270, 246 (1943).

[4] The following formulation appears to be a generalization of the specific quantitative formulation for the solvent extraction of zinc using dithizone given by KOLTHOFF and SANDELL (J. Amer. Chem. Soc. *63*, 1906 (1941).

[5] M. CALVIN and K. WILSON, J. Amer. Chem. Soc. *67*, 2003 (1945). – M. CALVIN and R. H. BAILES, J. Amer. Chem. Soc. *68*, 949 (1946). – R. B. DUFFIELD and M. CALVIN, J. Amer. Chem. Soc. *68*, 557 (1946). – M. CALVIN and N. C. MELCHIOR, J. Amer. Chem. Soc. *70*, 3270 (1948); J. Amer. Chem. Soc. *70*, 3273 (1948).

$$nKeH(o) \rightleftharpoons nKeH(w) \quad (4)$$

$$nKeH(w) \rightleftharpoons nKe^{-}(w) + nH^{+}(w) \quad (5)$$

$$Me^{+n}(w) + nKe^{-}(w) \rightleftharpoons MeKe_n(w) \quad (6)$$

$$MeKe_n(w) \rightleftharpoons MeKe_n(o) \quad (7)$$

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 affected 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[1]. 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[2] X—C(=O)—CH_2—C(=O)—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 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.

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Zusammenfassung

Eine allgemeine Methode für die Trennung von Metallen durch Verteilung zwischen zwei Lösungsmitteln wird beschrieben. Die Methode besteht in der Bildung von nichtionisierenden, und daher in organischen Lösungsmitteln löslichen Chelat-Verbindungen der Metalle mit bestimmten β-Diketonen. Die Trennung hängt von der Verschiedenheit mehrerer Eigenschaften der einzelnen metallischen Chelate ab. Die Grundlagen für die Auswahl der β-Diketone für bestimmte Metalle werden angegeben.

[1] The work described in this paper was sponsored by the Atomic Energy Commission.

[1] M. CALVIN and K. WILSON, J. Amer. Chem. Soc. *67*, 2003 (1945). – M. CALVIN and R. H. BAILES, J. Amer. Chem. Soc. *68*, 949 (1946). – R. B. DUFFIELD and M. CALVIN, J. Amer. Chem. Soc. *68*, 557 (1946). – M. CALVIN and N. C. MELCHIOR, J. Amer. Chem. Soc. *70*, 3270 (1948); J. Amer. Chem. Soc. *70*, 3273 (1948).

[2] J. C. REID and M. CALVIN, J. Amer. Chem. Soc., in press.

Polarographische Bestimmung der Komplexbildungskonstanten der Schwermetallkomplexe der Nitrilotriessigsäure[1]

Da eine direkte Bestimmung von Komplexbildungskonstanten der Nitrilotriessigsäure von größeren Werten als 10^8 aus den p_H-Titrationskurven anfänglich auf gewisse Schwierigkeiten stieß[2], versuchte I. KÖSSLER, diese Konstanten polarographisch zu bestimmen. Es hat sich gezeigt, daß die polarographische Stromspannungskurve der Lösungen von Metallsalzen bei der Anwesenheit von Nitrilotriessigsäure zwei Stufen zeigt, von denen die positivere der Reduktion der freien Metallionen, die zweite der direkten Reduktion des Komplexes zuzuschreiben ist. Unter der Voraussetzung, daß die Zerfall- und Bildungsgeschwindigkeiten des Komplexes nicht zu groß sind, entspricht die Höhe der ersten Reduktionsstufe der Konzentration der freien Metallionen in der Lösung. In diesem Falle wäre es möglich, die Komplexbildungskonstanten in einer gepufferten Lösung zu bestimmen, da

$$K_{MX} = \frac{[MX']}{[M^{++}]\cdot[X'''']} = \frac{[MX']\cdot[H^+]}{[M^{++}]\cdot[HX'']\cdot K_X} = \frac{(i_d - i_l)\cdot[H^+]}{i_l\left[c_s - c_m\left(1 - \frac{i_l}{i_d}\right)\right]K_X}$$

wo c_s die Gesamtkonzentration der Nitrilotriessigsäure, c_m die Gesamtkonzentration des Metallions, K_X die dritte Dissoziationskonstante der Nitrilotriessigsäure, i_l die Stufenhöhe der freien Metallionen bei der Anwesenheit von Nitrilotriessigsäure, i_d die Stufenhöhe bei der Abwesenheit von Nitrilotriessigsäure bezeichnet.

Bei den Versuchen wurde die Wasserstoffionenkonzentration durch Pufferlösungen von verschiedenem

[1] Diese Mitteilung stellt eine Zusammenfassung von Teilergebnissen der Dissertationen von Ivo KÖSSLER (1948) und JIŘÍ KORYTA (1949) dar. Beide Arbeiten werden gemeinsam in «Collection of Czechoslovak Chemical Communications» veröffentlicht werden.

[2] G. SCHWARZENBACH und W. BIEDERMANN, Helv. chim. acta *31*, 331 (1948).