Theory of Separating Columns

V. Zusammenfassung

Das Prinzip der physikalischen Altersbestimmung nach der "fission-track"-Methode wird erläutert. Experimentell wird ein schnelles und einfaches Verfahren zur Datierung von Gläsern ausgearbeitet. Die "fission-track"-Alter können auf 10% genau angegeben werden.

Approach to the Theory of Separating Columns with Successive Exchange between three Fluids

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Cohen's method has been used to develop the theory of continuous separating columns with successive exchange between three fluids. The equations of the column have been solved for stationary state and small concentrations. The general solutions representing the dependence of the mole fractions of the desired isotope in the three fluids on the column height involve the following particular cases: concurrent and countercurrent exchange between two fluids and two limiting cases of exchange between three fluids in which the intermediate fluid is at isotopic equilibrium with one of the other two fluids. As a general feature of the columns with successive exchange between three fluids it has been found that the ratio of the driving forces corresponding to the fluid pairs between which the mass-transfer takes place has a constant value along the column, excepting a zone situated at the bottom. Methods to calculate the rate constants from experimental data are given.

It is the purpose of this work to extend Cohen's theory to continuous separating columns in which the isotope transfer between the main fluids in countercurrent flow takes place indirectly, by means of a third fluid. This case, which will be referred to as "successive exchange" (Fig. 1 a), is only one of the possible cases of exchange between three fluids. The cases in which the mass transfer can take place simultaneously from the downflowing fluid to both upflowing fluids (simultaneous exchange, Fig. 1 b),
or in which the mass transfer takes place between all the three fluid pairs (complete exchange, Fig. 1 c) may also be considered and dealt with by the method used in this paper. Among them, the case of successive exchange has been chosen in this work because it differs mostly from the two fluid case considered by COHEN.

![Fig. 1. Mass transfer between three fluids, a) successive, b) simultaneous, c) complete.](image)

In practice even if the construction of a three fluid column may present more technical difficulties than a usual two-fluid one, the choice of a three-fluid system may be sometimes advantageous if the elementary separation factor defined for a fluid pair without direct isotope exchange has a large value. It may as well be sometimes preferable to combine in a three fluid system a distillation with small technical difficulties and a chemical exchange whereas the direct mass transfer from the gas to the liquid is not possible or occurs only at a negligibly small rate. The intermediate fluid consists therefore of the vapour of the liquid phase. The mass transfer rates $T_d$ and $T_s$ through the corresponding interfaces are defined for the unit height and the whole cross section of the column. The symbols introduced by COHEN shall be used together with $V$ for the vapour molal flow rate and $v$, the mole fraction of the considered isotope in the vapour phase. The subscripts s and d are used to denote chemical exchange and distillation. The positive direction of the $z$ axis along the column has been chosen inversely to that conventionally adopted by COHEN so that the enrichment of the considered isotope takes place at the $z = 0$ end of the column. The aim of this work is to establish the differential equations of the column for the stationary state and to solve them in the simplified case when the mole fractions of the considered isotope are small compared with unity.

The differential equations of the column may be obtained for the stationary state in the same way as it has been done by COHEN for two-fluid columns. The material balance written for an infinitesimal column element as shown in Fig. 2 leads to the system

$$
L \cdot \frac{dN}{dz} = -T_s,
V \cdot \frac{dV}{dz} = T_s - T_d,
L \cdot \frac{dL}{dz} = -T_d.
$$

According to COHEN the mass transfer rates $T_s$, $T_d$ may be written in the form

$$
T_s = k_s P_s [z_s n (1 - v) - v (1 - n)],
T_d = k_d P_d [z_d v (1 - N) - N (1 - v)],
$$

where the rate constants $k_s$, $k_d$ moles/cm$^2$·s refer to unit area of the corresponding interfaces, the mass transfer rates $T_s$, $T_d$ moles/cm$^2$·s corresponding to the unity of column height being therefore given by multiplication with the perimeters $P_s$, $P_d$ cm, of the corresponding interfaces. The molal flow rates $L$, $V$, $L$ moles/s refer to the whole section of the column.

A first consequence of the system (1) is the constant flux of isotope through any section of the column

$$
L n + V v - L N = \Omega, \text{ const.}
$$

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The system (1) has been solved to obtain the $z$-dependence of the mole fractions in the simplified case of small concentrations, $n, v, N \ll 1$. In this case the mass transfer rates (2) take the simplified form

$$T_s = k_s P_s (z_s n - v),$$
$$T_d = k_d P_d (z_d v - N),$$
and the system (1) becomes linear with constant coefficients.

Its general solution is:

$$n = A e^{-f_1 l z} + C e^{-f_2 l z},$$
$$v = z_s A + (z_s - f_1) B e^{-f_1 l z} + (z_s - f_2) C e^{-f_2 l z},$$
$$N = z_s A d + (V/L) (z_s + (l/V) - f_1) B e^{-f_1 l z}$$
$$+ (V/L) (z_s + (l/V) - f_2) C e^{-f_2 l z},$$

in which $A, B, C$ are arbitrary integration constants.

The symbols used have the following meaning:

$$\lambda = k_s P_s / l, \quad \text{cm}^{-1},$$
$$\mu = k_d P_d / L, \quad \text{cm}^{-1},$$
$$\eta = \mu / \lambda,$n
$$\gamma^* = \eta / (L z_s - V),$$

The difference between the solution (5) and the usual solutions that appear in two-fluid column theory consists in an additional exponential term; $f_1$ and $f_2$ are always real because the difference $1 - Q$ is always positive. In the solutions the rate constants are involved in the form of two parameters, $\lambda$ depending on the magnitude of a rate constant and $\eta$ only on their ratio. The roots $f_1$ and $f_2$ are depending only on the ratio of the rate constants.

The contribution of the two exponential terms depends on the values of $f_1$ and $f_2$; the analysis shows that for $\eta$ varying from 0 to $\infty$, $f_1$ increases from $z_s + l/V$ to $\infty$, whereas $f_2$ varies from 0 to $z_s - \gamma^*$, having the same sign as $z_s - \gamma^*$. Since the root $f_1$ is always positive, and $f_1 > f_2$, the behaviour of the functions is determined at small values of $z$ by the first exponential term $e^{-f_1 l z}$, whereas the second term $e^{-f_2 l z}$ becomes essential at large $z$ values. For small values of $Q, Q \ll 1$, the roots $f_1$ and $f_2$ are approximately given by

$$f_1 \approx f_1^* = z_s + (l/V) (1 + \eta / \gamma^*),$$
$$f_2 \approx f_2^* = f_2^* + (l/V) (1 + \eta / \gamma^*).$$

The integration constants $A, B, C$ may be determined by means of three arbitrarily chosen concentration values. In terms of $n_0, v_0$ and $N_0$, the mole fractions of the considered isotope at the end $z = 0$ of the column, the constants $A, B, C$ may be expressed as follows:

$$A = \frac{\gamma^*}{z_s - \gamma^*} L_{N_0 - l n_0 - v v_0},$$
$$B = - \frac{f_1^* \gamma^*}{(f_1 - f_2) (z_s - \gamma^*)} L \left( z_s v_0 - N_0 \right)$$
$$+ \frac{z_s - \gamma^* - f_2}{(f_1 - f_2) (z_s - \gamma^*)} \left( z_s n_0 - v_0 \right),$$
$$C = \frac{f_2^* \gamma^*}{(f_1 - f_2) (z_s - \gamma^*)} L \left( z_s v_0 - N_0 \right)$$
$$+ \frac{f_1^* - (z_s - \gamma^*)}{(f_1 - f_2) (z_s - \gamma^*)} \left( z_s n_0 - v_0 \right).$$

The general solution (5) permits to find again the equations of concurrent and countercurrent exchange between two fluids. Besides these cases encountered in the theory of two-fluid columns there are also two particular cases of exchange between three fluids.

Case a) The vapour-liquid exchange is much faster than the vapour-gas exchange. In this case $\eta \gg \lambda, \eta \rightarrow \infty$ and therefore $f_1 \rightarrow \infty, f_2 \rightarrow z_s - \gamma^*$. If an additional condition $z_s v_0 = N_0$ is given, i.e. if the column is fed at the bottom with vapour at isotopic equilibrium with the liquid, then the following equations may be derived from (5) and (13):

$$n = \frac{\gamma^* n_0 - z_s n_0 - v v_0 e^{-(z_s - \gamma^*) l z}}{z_s - \gamma^*},$$
$$v = \frac{z_s n_0 - v_0 e^{-(z_s - \gamma^*) l z}}{z_s - \gamma^*},$$
$$N = z_s v.$$

In every point of the column the vapour will be at isotopic equilibrium with the liquid. The behaviour of the three fluid systems is analogous to a two fluid system in countercurrent flow with a separation factor $z_s$, flow rates $l$ and $L z_s - V$ and the conservation of isotope given by

$$(L z_s - V) (N/z_s) - l n = \text{const.}.$$
\[ f_1 = \alpha_s + l/V, \quad f_2 = 0, \quad \lambda f_1 \to \infty, \]
\[ \lambda f_2 = \frac{L \mu}{l + V \alpha_s} \left( \alpha_s \alpha_d - \frac{1 + V \alpha_s}{L} \right) \]


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\[ \text{together with the condition } \alpha_s n_0 = r_0 \text{ (the column is fed with vapour and gas at isotopic equilibrium) the solutions take the form} \]
\[ n = \frac{N_s - K n_0}{\alpha_s \alpha_d - K} + \frac{\alpha_s \alpha_d - N_0}{\alpha_s \alpha_d - K} \cdot \exp \left\{ -\frac{\mu}{K} (\alpha_s \alpha_d - K) z \right\}, \]
\[ v = \alpha_s n, \]
\[ N = \frac{\alpha_s \alpha_d n_0 - K n_0}{\alpha_s \alpha_d - K} + \frac{K \frac{\alpha_s \alpha_d - N_0}{\alpha_s \alpha_d - K} \cdot \exp \left\{ -\frac{\mu}{K} (\alpha_s \alpha_d - K) z \right\}, \]
\[ K \equiv \frac{(l + V \alpha_s)}{L}. \]


\[ \text{In this case there is isotopic equilibrium between the vapour and the gas at any height of the column. The isotope conservation equation is} \]
\[ L N - (l + V \alpha_s) n = \text{const}. \]

The three fluid system is equivalent to a two fluid system in countercurrent flow characterized by the mole fractions \( n \) and \( N \), the flow rates \( L \) and \( l + V \alpha_s \) and a separation factor of \( \alpha_s \alpha_d \).

In both cases if at the bottom of the column the conditions \( \alpha_d n_0 = N_0 \) and \( \alpha_s n_0 = r_0 \) are not fulfilled then in (14) and (15) there are also present additional terms that make the differences \( \alpha_d v - N \) and \( \alpha_s n - v \) to decrease rapidly with \( e^{-\lambda z} \).

The case of a real three fluid system lies between the limiting cases a) and b). The extent to which it approaches one of these cases depends upon the value of \( q \). For \( q \to 0 \) the mole fractions in the gas and vapours tend to approach equilibrium (case b) whereas for \( q \to \infty \) the approach to equilibrium of the mole fractions takes place between the liquid and vapour.

The driving forces (the distances from the equilibrium)
\[ \Delta_s = \alpha_s n - v, \quad \Delta_d = \alpha_d v - N \]

may be obtained in the general case using Eqs. (5):
\[ \Delta_s = f_1 B e^{-f_1 \lambda z} + f_2 C e^{-f_2 \lambda z}, \]
\[ \Delta_d = \frac{l}{\gamma^* L} \left[ (\alpha_s - \gamma^* - f_1) B e^{-f_1 \lambda z} + (\alpha_s - \gamma^* - f_2) C e^{-f_2 \lambda z} \right]. \]

The values \( \Delta_s, \Delta_d \) vary first rapidly with \( z \) in virtue of the \( e^{-f_1 \lambda z} \) exponential term; then beyond a \( z = z_0 \) value the first exponential term becomes negligible, \( e^{-f_1 \lambda z_0} \ll e^{-f_2 \lambda z} \).

The case of a real three fluid system lies between the limiting cases a) and b). The extent to which it approaches one of these cases depends upon the value of \( q \). For \( q \to 0 \) the mole fractions in the gas and vapours tend to approach equilibrium (case b) whereas for \( q \to \infty \) the approach to equilibrium of the mole fractions takes place between the liquid and vapour.

Besides the computation of the concentration profiles if the \( q \) and \( \lambda \) values are known it is also of interest to solve the problem inversely, that is to determine the values of the parameters \( q \) and \( \lambda \) if the values of the mole fractions at both ends of the column are experimentally known.

By eliminating \( C e^{-\lambda I \lambda z} \) from the first two equations (5) written for \( z = Z \) and by using Eq. (3) it may be shown that
\[ \frac{f_2}{f_2} = \left( \alpha_s - \gamma^* \right) \frac{\Delta_s(Z) - R}{\Delta_d(Z) + \Delta_s(Z)} \]
\[ \text{where} \quad R = (f_1 - f_2) B e^{-f_1 \lambda z} \]
and where \( \Delta_s(Z) = \alpha_s n - v_z, \Delta_d(Z) = \alpha_d v - N_z \) are the driving forces at the top of the column. By solving Eq. (18) with respect to \( q \) one obtains

\[ Q = \frac{\Delta_s(Z) - R}{\Delta_d(Z) + (l/\gamma^* L) R} \left[ \frac{l + V \alpha_s}{L} - \frac{V(\alpha_s - \gamma^*)}{L^2} \right] \frac{\Delta_s(Z) - R}{\Delta_d(Z) + (l/\gamma^* L) \Delta_s(Z)} . \]

Similarly starting from the first of Eq. (5) it may be shown that
\[ \lambda = \frac{1}{f_2 Z} \ln \frac{f_1 (\gamma^* L/l) \Delta_{d0} + (f_1 - \alpha_s + \gamma^*) \Delta_{s0}}{(f_1 - f_2) [(\gamma^* L/l) \Delta_d(Z) + \Delta_s(Z)] - (\alpha_s - \gamma^*)} . \]

The Eqs. (20) and (21) are implicit in \( q \) and \( \lambda \) since \( R \) contains both \( q \) and \( \lambda \). This difficulty may however be avoided by a proper choice of the height \( Z \) of the column. If \( Z \) is sufficiently large \( R \) becomes negligibly small and permits the direct computation of \( q \) and \( \lambda \). If the experimental conditions don’t per-
mit to make $R \approx 0$, then the Eqs. (20) and (21) have to be solved by successive approximations, starting with $R = 0$ for the first approximation of $\phi$ and $\lambda$, then computing $R$ from Eq. (19) in order to obtain the second approximation, etc. The rate constants $k_s, k_d$ may finally be determined from Eqs. (6) – (8).

Conclusions

1. By the extension of Cohen's theory to separating columns with successive exchange between three fluids it is possible both to determine the dependence of the mole fractions on the height of the column from known values of the rate constants, and to compute the rate constants if the values of the mole fractions at the ends of the column are known.

2. The specific feature of columns with successive exchange between three fluids consists in the height dependence of the mole fractions in the form of two exponential terms with unequal exponents. Excepting a zone situated at the bottom of the column, $z \approx 0$, the mole fractions vary along the column so that the ratio of the driving forces remain constant.

On the Dissociation of Silver, Thallium and Zinc Sulphates in Some Molten Nitrates*

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The cryoscopic behaviour of Ag, Tl and Zn sulphates in a number of molten univalent nitrates has been investigated. $\text{Ag}_2\text{SO}_4$ appears to be thoroughly ionized in LiNO$_3$ and partially ionized in KNO$_3$; $\text{Tl}_2\text{SO}_4$ thoroughly in Li, Na and Ag nitrates; $\text{ZnSO}_4$ thoroughly in LiNO$_3$ and partially in Na, K and Ag nitrates.

The present paper aims at inquiring the ionization of some sulphates when dissolved in molten nitrates having suitable characteristics, and of which heats of fusion and cryoscopic constants were already well known. The solutions of $\text{Ag}_2\text{SO}_4$ in LiNO$_3$ and KNO$_3$, of $\text{Tl}_2\text{SO}_4$ in LiNO$_3$, NaNO$_3$, and AgNO$_3$ and of $\text{ZnSO}_4$ in LiNO$_3$, NaNO$_3$, KNO$_3$, and AgNO$_3$ have been chosen.

A previously described conventional cryoscopic apparatus has been employed. All salts (C. Erba RP, Merck "pro analysi" or BDH) have been carefully dried before use.

The experimental results are shown in Figs. 1 – 3. A number of numerical data, interpolated from the experimental ones and used in the following discussion, are summarized in Table 1.

Discussion

The possibility of evaluating cryoscopically active species $v$ and, in general, of applying the cryoscopic method is usually conditioned to the fact that solute and solvent do not form solid solutions. In order to ascertain this point in the systems here involved,

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<th>System</th>
<th>$m = 0.04$</th>
<th>0.06</th>
<th>0.08</th>
<th>0.10</th>
<th>0.12</th>
<th>0.14</th>
<th>0.16</th>
<th>0.18</th>
<th>0.20</th>
<th>0.22</th>
<th>0.24</th>
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<tr>
<td>$\text{Ag}_2\text{SO}_4$ in KNO$_3$</td>
<td>3.43</td>
<td>5.02</td>
<td>6.56</td>
<td>8.09</td>
<td>9.53</td>
<td>10.91</td>
<td>11.67</td>
<td>11.95</td>
<td>12.08</td>
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<tr>
<td>$\text{Ag}_2\text{SO}_4$ in (KNO$_3$+0.10m.AgNO$_3$)</td>
<td>3.23</td>
<td>4.78</td>
<td>6.27</td>
<td>7.69</td>
<td>9.04</td>
<td>10.37</td>
<td>10.67</td>
<td>11.05</td>
<td>11.26</td>
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<tr>
<td>$\text{Ag}_2\text{SO}_4$ in (KNO$_3$+0.25m.AgNO$_3$)</td>
<td>3.05</td>
<td>4.49</td>
<td>5.92</td>
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<td>$\text{ZnSO}_4$ in NaNO$_3$</td>
<td>1.92</td>
<td>2.35</td>
<td>2.75</td>
<td>3.13</td>
<td>3.47</td>
<td>3.81</td>
<td>4.12</td>
<td>4.44</td>
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<td>2.13</td>
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<tr>
<td>$\text{ZnSO}_4$ in (NaNO$_3$+0.119m.Na$_2$SO$_4$)</td>
<td>1.47</td>
<td>1.79</td>
<td>2.09</td>
<td>2.39</td>
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<td>2.99</td>
<td>3.27</td>
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Table 1. $\Delta T_{\text{exp}}$ (°C) interpolated values for partially ionized sulphates.

* Work carried out with the help of the Consiglio Nazionale delle Ricerche (Rome).