Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Lodato, Vincent A.(1972) 'Competitive Processes for Isotopic Separation in the Solid Phase', Separation Science and Technology, 7: 4, 319 — 329
To link to this Article: DOI: 10.1080/00372367208055576
URL: http://dx.doi.org/10.1080/00372367208055576

SEPARATION SCIENCE, 7(4), pp. 319–329, 1972

Competitive Processes for Isotopic Separation in the Solid Phase

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Abstract

The kinetic scheme for the photo-isotopic separation of uranium is discussed. The effect of different processes on the efficiency is demonstrated and it is shown that the addition of a quencher enchances the selectivity but decreases the efficiency of the process.

INTRODUCTION

In an idealized photochemical isotopic separation scheme the desired isotopic species is excited with the complete exclusion of excitation of undesired species, and each excited species results in the formation of a separable reaction product. This idealization leads to complete separation of the desired isotope in pure form.

In this paper we present a formal analysis of the consequences of recognized sources of deviation from the ideal model for the case of a solid state oxidation–reduction process. The approach used is to treat the desired ideal process and deviations as a system of competing kinetic processes. Within the approximations taken, the resulting system of differential equations is solved in closed form.

For comparison with existing and alternative processes of separation, the results of the computation have been used to calculate enrichment

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factors. For evaluation of a practical system it is also necessary to consider the energy requirement which is dependent on the effective quantum yield. As will be seen, the case of adequate selectivity is achieved by the addition of a quencher to the system.

MODEL

Isotopic species are designated as A and B; A being the desired isotope. In the over-all reaction A or B may react with X to form final product A^- or B^-, which is assumed to be separable from the starting material without isotope exchange. The processes considered and their formal rate expressions are set forth as follows.

1. Initial excitation of A:

$$A \xrightarrow{h\nu} A^*$$

$$r_1 = k_1(A)$$

i.e., the process is treated as first order in the concentration of A, the value of k being a function of the absorption coefficient and the intensity of the illuminating source. In carrying out formal calculations the positional dependence of the light intensity due to absorption is not considered.

$$B \xrightarrow{h\nu} B^*$$

$$r_1' = k_1'(B)$$

Ideally, $k' = 0$, i.e., there is no absorption by the unwanted isotope, but k may be finite because of line broadening either in the absorber or source, or as a result of degradation of the monochromatic light by imperfection of the absorber.

2. Fluorescent decay:

$$A^* \rightarrow A + h\nu$$

$$B^* \rightarrow B + h\nu$$

$$r_2 = k_2(A^*)$$

$$r_2' = k_2(B^*)$$

k_1, k_1', and k_2 are treated as independent but are in fact related through the radiative lifetime.

3. Excitation transfer (*1*):

$$A^* + B \rightarrow A + B^*$$

$$r_3 = k_3(A^*)$$

It is assumed that (B) ≫ (A). From this it follows that the reverse reaction can be ignored. k_3 is in principle dependent on (B) (*1*) but the functionality is difficult to estimate for a reacting solid. The greatest error is to be expected where high conversion to B^- occurs via direct absorption by B, in which case k_3 will be overestimated.

4. Radiationless deactivation:

$$A^* \rightarrow A + \Delta H$$

$$B^* \rightarrow B + \Delta H$$

$$r_4 = k_4(A^*)$$

$$r_4' = k_4(B^*)$$

In terms of solution of the kinetic equations this process is not distinguishable from fluorescent decay and, indeed, terms will only appear in the form $(k_2 + k_4)$. The distinction does provide for the consideration of observed temperature dependence of fluorescent yield (*2*), where the deviation from a yield of 1 is attributed to radiationless deactivation.

5. Charge transfer:

$$A^* + X \rightarrow A^-$$

$$B^* + X \rightarrow B^-$$

$$r_5 = k_5(A^*)$$

$$r_5' = k_5(B^*)$$

Treating the charge transfer reaction as first order in the activated species and independent of (X), which is consumed, should be valid at low conversions but can be expected to fail in a process carried to complete conversion. If the charge transfer is intramolecular, any unreacted A or B should still be adjacent to X, i.e., the system is not random so the assumption that the rate is independent of (X) is more reasonable than a first-order dependence on (X).

All of the rate constants are treated as time and conversion invariant. This approximation should be reasonable for highly selective cases and in general near the beginning of conversion.

Based on these rate expressions the following set of differential equations can be written:

$$d(\mathrm{A})/dt = -k_1(\mathrm{A}) + (k_2 + k_3 + k_4)(\mathrm{A}^*) \tag{1}$$

$$d(\mathrm{A}^*)/dt = k_1(\mathrm{A}) - (k_2 + k_3 + k_4 + k_5)(\mathrm{A}^*) \tag{2}$$

$$d(\mathrm{A}^-)/dt = k_5(\mathrm{A}^*) \tag{3}$$

$$d(\mathrm{B})/dt = -k_1(\mathrm{B}) - k_3(\mathrm{A}^*) + (k_2 + k_4)(\mathrm{B}^*) \tag{4}$$

$$d(\mathrm{B}^*)/dt = k_2(\mathrm{B}) + k_3(\mathrm{A}^*) - (k_2 + k_4 + k_5)(\mathrm{B}^*) \tag{5}$$

$$d(\mathrm{B}^-)/dt = k_5(\mathrm{B}^*) \tag{6}$$

This set of equations is soluble in closed form. The Laplace transform technique can be applied, and the resulting populations are:

$$\mathrm{A}(t) = \frac{\mathrm{A}(0)}{\lambda_2 - \lambda_1}\left[(\lambda_2 + k_2)e^{\lambda_1 t} - (k_1 + \lambda_1)e^{\lambda_2 t}\right] \tag{7}$$

$$\mathrm{A}^*(t) = \frac{\mathrm{A}(0)(k_1 + \lambda_1)(k_1 + \lambda_2)}{(\lambda_2 - \lambda_1)(k_2 + k_3 + k_4)}\left(e^{\lambda_1 t} - e^{\lambda_2 t}\right) \tag{8}$$

$$\begin{aligned}\mathrm{A}^-(t) = \mathrm{A}(0)\Bigg\{1 &+ \frac{1}{(\lambda_2 - \lambda_1)(k_2 + k_3 + k_4)} \\ &\times \left[-(k_1 + \lambda_2)(k_1 + k_2 + k_3 + k_4 + \lambda_1)e^{\lambda_1 t}\right. \\ &\left.+ (k_1 + \lambda_1)(k_1 + k_2 + k_3 + k_4 + \lambda_2)e^{\lambda_2 t}\right]\Bigg\}\end{aligned} \tag{9}$$

$$\begin{aligned}B(t) = &\frac{B(0)}{\lambda_4 - \lambda_3}\left[(\lambda_4 + k_1')e^{\lambda_3 t} - (k_1' + \lambda_3)e^{\lambda_4 t}\right] \\ &+ k_3 A(0)\frac{(k_1 + \lambda_1)(k_2 + \lambda_2)(k_2 + k_4)}{(\lambda_2 - \lambda_1)(k_2 + k_3 + k_4)\delta\beta} \\ &\times\left[-(k_1' - k_2 - k_4 + \lambda_4)\frac{e^{\lambda_1 t} - e^{\lambda_3 t}}{\lambda_1 - \lambda_3}\right. \\ &\left.+ (k_1' + k_2 + k_4 + \lambda_3)\frac{e^{\lambda_1 t} - e^{\lambda_4 t}}{\lambda_1 - \lambda_4} - \frac{e^{\lambda_2 t} - e^{\lambda_4 t}}{\lambda_2 - \lambda_4}\right]\end{aligned} \tag{10}$$

$$B^*(t) = \frac{B(0)(k_1' + \lambda_3)(k_1' + \lambda_4)}{(\lambda_4 - \lambda_3)(k_2 + k_4)} (e^{\lambda_3 t} - e^{\lambda_4 t})$$

$$+ k_3 A(0) \frac{(k_1 + \lambda_1)(k_2 + \lambda_2)}{(\lambda_2 - \lambda_1)(k_2 + k_3 + k_4)\delta\beta}$$

$$\times \left[(k_1' + \lambda_4)(k_1' + k_2 + k_4 + \lambda_3) \left(\frac{e^{\lambda_1 t} - e^{\lambda_4 t}}{\lambda_1 - \lambda_4} - \frac{e^{\lambda_2 t} - e^{\lambda_4 t}}{\lambda_2 - \lambda_4} \right) \right.$$

$$\left. - (k_1' + \lambda_3)(k_1' + k_2 + k_4 + \lambda_4) \left(\frac{e^{\lambda_1 t} - e^{\lambda_3 t}}{\lambda_1 - \lambda_3} - \frac{e^{\lambda_2 t} - e^{\lambda_3 t}}{\lambda_2 - \lambda_3} \right) \right] \tag{11}$$

The population of the $B^-(t)$ is

$$B^-(t) = B(0) \left\{ 1 + \frac{1}{(\lambda_4 - \lambda_2)(k_2 + k_4)} \right.$$

$$\times \left[- (k_1' + \lambda_4)(k_1' + k_2 + k_4 + \lambda_3) e^{\lambda_3 t} \right.$$

$$+ (k_1' + \lambda_3)(k_1' + k_2 + k_4 + \lambda_4) e^{\lambda_4 t}$$

$$\left. - \frac{k_3 A(0)(k_1 + \lambda_1)(k_2 + \lambda_2)}{(\lambda_2 - \lambda_1)(k_2 + k_3 + k_4)\delta\beta} \right] \left\{ \left[\frac{e^{\lambda_1 t} - e^{\lambda_3 t}}{\lambda_1 - \lambda_3} - \frac{e^{\lambda_2 t} - e^{\lambda_3 t}}{\lambda_2 - \lambda_3} \right] \right.$$

$$\times [- (k_1' + \lambda_3)(k_1' + k_2 + k_4 + \lambda_4)$$

$$+ (k_2 + k_4)(k_2 + k_4 - k_1' - \lambda_4)] + \left[\frac{e^{\lambda_1 t} - e^{\lambda_4 t}}{\lambda_1 - \lambda_4} - \frac{e^{\lambda_2 t} - e^{\lambda_4 t}}{\lambda_2 - \lambda_4} \right]$$

$$\left. \left. \times [(k_1' + k_2 + k_4 + \lambda_3)(k_1' + k_2 + k_4 + \lambda_4)] \right\} \right\} \tag{12}$$

where

$$\lambda_1 = -\frac{1}{2} \sum_{i=1}^{5} k_i + \tfrac{1}{2} \{ (k_2 + k_3 + k_4 + k_5 - k_1)^2 + 4k_1(k_2 + k_3 + k_4) \}^{1/2}$$

$$\lambda_2 = -\frac{1}{2} \sum_{i=1}^{5} k_i - \tfrac{1}{2} \{ (k_2 + k_3 + k_4 + k_5 - k_1)^2 + 4k_1(k_2 + k_3 + k_4) \}^{1/2}$$

$$\lambda_3 = -\frac{1}{2}\left(k_1' + \sum_{i=2}^{5} k_i\right) + \tfrac{1}{2}\{(k_2 + k_4 + k_5 - k_1')^2 + 4k_1(k_2 + k_4)\}^{1/2}$$

$$\lambda_4 = -\frac{1}{2}\left(k_1' + \sum_{i=2}^{5} k_i\right) - \tfrac{1}{2}\{(k_2 + k_4 + k_5 - k_1')^2 + 4k_1'(k_2 + k_4)\}^{1/2}$$

$$\delta = \{(k_2 + k_4)^2 + (k_1' + \lambda_3)^2\}^{1/2}$$

$$\beta = \{(k_2 + k_4)^2 + (k_1' + \lambda_4)^2\}^{1/2}$$

It should be noted that the eigenvalues are real and negative. This establishes the asymptotic stability of our solution. It is quite evident that the solutions are cumbersome.

In order to simplify the solutions, the assumption is made that the primary activation is much slower than any other process proceeding at a finite rate. The system of equations is then in a pseudo-steady-state condition with

$$dA^*/dt \approx 0 \tag{13}$$

$$dB^*/dt \approx 0 \tag{14}$$

Under these conditions Eqs. (7) and (9) can be solved to give

$$A(t) = A(0)e^{-at} \tag{15}$$

$$A^-(t) = A(0)(1 - e^{-at}) \tag{16}$$

where

$$a = \frac{k_1k_5}{k_2 + k_3 + k_4 + k_5}$$

and Eqs. (11) and (12) become

$$B(t) = B(0)e^{-bt} + \frac{k_1k_3A(0)}{(k_1' - k_1)(k_2 + k_4 + k_5) + k_1'k_3}[e^{-bt} - e^{-at}] \tag{17}$$

$$B^-(t) = B(0)(1 - e^{-bt}) + \frac{k_1k_3A(0)}{(k_1 - k_1')(k_2 + k_4 + k_5) - k_1'k_3}[e^{-bt} - e^{-at}] \tag{18}$$

$$b = \frac{k_1'k_5}{k_2 + k_4 + k_5}$$

From the steady-state hypothesis one has

$$A^*(t) = \frac{k_1 A(0) e^{-at}}{k_2 + k_3 + k_4 + k_5} \tag{19}$$

and also a corresponding expression for $B^*(t)$.

It can be shown that the exact solutions approach the steady-state approximations under the conditions that $k_1 \ll (k_2 + k_3 + k_4 + k_5)$ and $t \gg (k_2 + k_3 + k_4 + k_5)^{-1}$.

DISCUSSION

The separation factor α, defined as the ratio of the isotope ratio of the product to that of the waste (*2*), can be used to examine the consequences of the competitive processes on selectivity. For an ideal gaseous diffusion process $\alpha = M_2/M_1$ or, for UF_6, $\alpha = 1.004$.

In the present notation

$$\alpha = \frac{(A^-)/(B^-)}{(A)/(B)} = \frac{(A^-)}{(A)} \frac{(B)}{(B^-)} \tag{20}$$

A photochemical process can be carried to completion. Then $(A) \rightarrow 0$ and α becomes undefined in the limit. For this reason it is useful to also consider the heads separation factor β (*3*), given by

$$\beta = \frac{(A)}{(B)} \frac{(B_0)}{(A)} \tag{21}$$

The complete expressions for species concentrations are complex even with the steady-state approximations. Therefore, two limiting cases are considered.

1. $k_3 = 0$, i.e., no excitation transfer. Substituting into Eq. (20) from Eqs. (15)–(18)

$$\alpha = (e^{at} - 1)/(e^{bt} - 1) \tag{22}$$

where $a = k_1(k_5/k_2 + k_4 + k_5)$ since $k_3 = 0$. The initial α is k_1/k_1'. At large t, α diverges since $a > b$. Similarly

$$\beta = (1 - e^{-at})/(1 - e^{-bt}) \tag{23}$$

Again at $t = 0$, $\beta = k_1/k_1'$, but the limit at long times is $\beta = 1$. Since the conversions of A and B are going independently, this is the expected result. At long enough time the material will be fully converted with no enrichment relative to the starting material

2. $k_1' = 0$:

$$\alpha = \left[\frac{B_0}{A_0}\,\frac{k_2 + k_4 + k_5}{k_3} - 1\right] e^{at} + 1 \tag{24}$$

TABLE 1

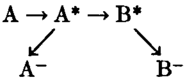
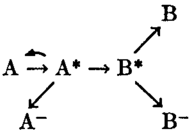
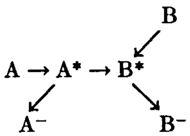
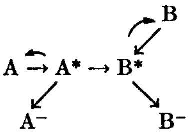
	SCHEME	k_1	k_2	k_3	k_4	k_5	k_1'
(1)	$A \rightarrow A^* \rightarrow A^-$	10^{-3}	0.0	0.0	0.0	100	0.0
(2)	$A \rightleftarrows A^* \rightarrow A^-$	10^{-3}	50	0.0	50	100	0.0
(3)	$A \rightarrow A^* \rightarrow A^-$ $B \rightarrow B^* \rightarrow B^-$	10^{-3}	0.0	0.0	0.0	100	10^{-4}
(4)	$A \rightleftarrows A^* \rightarrow A^-$ $B \rightleftarrows B^* \rightarrow B^-$	10^{-3}	50	0.0	50	100	10^{-4}
(5)		10^{-3}	0.0	100	0.0	100	0.0
(6)		10^{-3}	50	100	50	100	0.0
(7)		10^{-3}	0.0	100	0.0	100	10^{-4}
(8)		10^{-3}	50	100	50	100	10^{-4}

TABLE 2

Enrichment and Conversion as Functions of Time[a]

	Case I		Case II		Case III		Case IV	
Time	C(%)	E(%)	C(%)	E(%)	C(%)	E(%)	C(%)	E(%)
0	0	—	0	—	0	—	0	—
10^3	63	100	39	100	63	6.29	39	7.54
2×10^3	86	100	63	100	86	4.60	63	6.29
3×10^3	95	100	78	100	95	3.57	78	5.33
4×10^3	98	100	86	100	98	2.92	86	4.60
5×10^3	99.3	100	92	100	99.3	2.49	92	4.02
6×10^3	99.7	100	95	100	99.7	2.18	95	3.57
7×10^3	99.9	100	97	100	99.9	1.96	97	3.21
8×10^3	99.996	100	98	100	99.996	1.80	98	2.92
	Case V		Case VI		Case VII		Case VIII	
0	0	—	0	—	0	—	0	—
10^3	39	50.0	26	66.0	39	3.91	26	6.20
2×10^3	63	50.0	45	66.0	63	3.36	45	4.30
3×10^3	78	50.0	59	66.0	78	2.92	59	4.10
4×10^3	86	50.0	70	66.0	86	2.57	70	3.78
5×10^3	92	50.0	78	66.0	92	2.30	78	3.45
6×10^3	95	50.0	83	66.0	95	2.08	83	3.12
7×10^3	97	50.0	88	66.0	97	1.91	88	2.88
8×10^3	98	50.0	91	66.0	98	1.77	91	2.71

[a] C ≡ % conversion of A to $A^-(=A^-/A_0)$. E ≡ % enrichment of product $(=A^-/(A^- + B^-))$. Enrichment of starting material = 1%. Time in arbitrary units.

This result indicates that the separation factor increases with lower grade feed. The enrichment also increases with time provided that

$$\alpha = \left[\frac{B_0}{A_0}\frac{k_2 + k_4 + k_5}{k_3} - 1\right]\frac{A_0}{A} + 1 \tag{25}$$

where the long time divergence can be seen to arise as A → 0.

$$\beta = \frac{k_2 + k_4 + k_5}{k_3}\frac{B_0}{A_0} \tag{26}$$

Again the feed dependence is clear.

The results for both α and β show the intuitive result that if k_3 is excessively large, an enrichment <1 can result.

A surprising consequence in both α and β for $k_1' = 0$ is that fluorescent decay and radiationless transfer improve the selectivity.

The time dependence of reactant and product concentrations has been calculated using the exact solution for eight combinations of rate constants. The values used are set forth in Table 1. The initial concentrations were taken as $A_0 = 1$ and $B_0 = 100$. Table 2 shows the results in terms of the enrichment of the product, i.e., $A^-/(A^- + B^-)$, and the fractional conversion of A.

The values of the constants selected for the numerical evaluation is arbitrary and serves to illustrate the consequences of the competing processes. It is possible to make some order of magnitude statements regarding time constants.

k_1 is a function of absorption coefficient and light intensity. It can be assumed that treatment times would be of the order of seconds to hours so that the effective k_1 might range from 1 to 10^{-4} sec^{-1}. In the event of low efficiency larger values, i.e., more intense illumination, would be required to maintain feasible processing time.

From the results of Hall and Dieke (*4*) on the low temperature fluorescent of uranyl salts, k_2 is of the order 10^3 sec^{-1}. At liquid hydrogen the same work suggests a radiationless decay constant, i.e., k_4, of the same order.

From the investigation of the excitation transfer process (*1*), k_3 can be expected to be of the order of $>10^5$ sec^{-1} in systems of reasonable concentration, i.e., dilutions of 100 or less. This high rate is the basis for the preliminary assertion that a process that is adequately selective must be efficient with respect to fluorescent and radiationless transfer. The results of the analysis suggest that a deliberate departure from this condition might be desirable.

As can be seen from Eqs. (24) and (26), the enrichment factor is improved by increasing values of k_2 and k_4. The deliberate addition of a quenching material to increase k_4 will thus improve selectivity at the cost of efficiency.

From Eq. (26) it can be seen that if k_5 is not more than an order of magnitude smaller than k_3, enrichments of the order of 10% starting with natural uranium feed would be achieved, provided the photo selectivity of primary absorption were maintained. If quenching were also involved, $k_5 \sim 10^3$ sec^{-1} would provide a selective process of limited efficiency.

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Received by editor October 29, 1971