RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

May 1975

Translated from *Uspekhi Khimii*, **43**, 761-781 (1975)

U. D. C. 546.791.02

Chemical Separation of Uranium Isotopes

B.N.Laskorin, A.M.Babenko, E.A.Filippov, and A.F.Trubnikov

A brief survey is made of published work on various methods (electrochemical, chemical, extraction, and ion exchange) for separating the uranium isotopes 235 and 238. Attention is paid mainly to ion exchange using different states of oxidation of uranium in aqueous and organic solutions. The bibliography contains 70 references.

CONTENTS

I. Introduction 381
II. Brief historical survey of chemical methods for separating uranium isotopes 381
III. Separation of uranium isotopes by ion exchange 382

I. INTRODUCTION

The separation of isotopes is based on differences in their physical and chemical properties. Since such differences are small, and diminish with increase in the atomic number of the element, the separation of isotopic mixtures is a very difficult task. Differences in the properties of isotopic varieties are obviously due to the difference in their masses.

Only physical methods—gas diffusion and centrifuging—have been developed for the industrial separation of uranium isotopes[1]. In several countries research has now been started with the aim of developing chemical methods for separating the isotopes of uranium.

II. BRIEF HISTORICAL SURVEY OF CHEMICAL METHODS FOR SEPARATING URANIUM ISOTOPES

During recent years several researches have been published in the foreign periodical press on chemical methods for separating uranium isotopes. Such methods can be classified as (i) electrochemical, (ii) chemical exchange in aqueous solution, (iii) extraction, and (iv) ion exchange. Work on the chemical separation of uranium isotopes was begun and continued during the Second World War by Brewer and Madorsky[2] using countercurrent electrical migration, which involved a difference in the kinetic properties of the ions. Their results were published towards the end of the 1940s.[3,4] In 1953 these workers reported briefly[5] that they had used ionic mobilities to enrich uranium with the light isotope from 0.72% to 2.8%.

A process for fractionating uranium isotopes, patented by Woodward[6] in 1957, was based on isotopic exchange between uranium(IV) and uranium(VI) ions in an acidic aqueous solution. In such solutions the quadrivalent ions become enriched with uranium-238, and the sexivalent ions with uranium-235. When two or more isotopes are present in solution, those of highest atomic weight tend to concentrate in the lower state of oxidation, and the others in the higher state. Woodward conducted isotopic exchange in aqueous hydrochloric acid containing 2% each of uranium(IV) and uranium(VI) (pH 1.5–1.9 for 1 h); after the exchange uranium(IV) was precipitated as the dioxalate, which after several intermediate operations was converted into the tetrachloride and used in the preceding stage of the process, while the filtrate was transformed into uranyl chloride, which was submitted to the following stage of

enrichment. This process of chemical enrichment is difficult to adapt to multistage working, since it involves many intermediate operations (precipitation, filtration, ignition).

Twitchell, Williams, and Clark[7] concentrated uranium-235 by chemical exchange combined with counterflow electrical migration: uranium(IV) and uranium(VI) moved in opposite directions on the latter principle, whose application had given good results in concentrating potassium, chlorine, and copper isotopes. It was shown that uranium(IV) could be transported from cathode to anode by the electrolyte flowing countercurrent to the uranium(VI) migrating to the cathode. After the cell had operated for 1400 h the uranium-235 content had increased from 0.7111% to 0.7171%. However, it was admitted[7] that this method involved many technical difficulties.

A 1958 patent[8] described a chemical method of isotopic fractionation of uranium based on extraction. This started from the suggestion[9] that the achievement of efficient separation entailed that the chemical state of an isotope in the organic phase should differ from its chemical state in the aqueous phase. This requirement was satisfied by a system in which a metal ion in the aqueous phase was in equilibrium with a chelate or other complex of the metal in an organic solvent immiscible with the aqueous solution. It was established that isotopic exchange took place when an acidic aqueous solution of uranium(IV) was in contact with a water-immiscible organic solvent in which was dissolved a water-insoluble chelate complex of uranium(IV), as a result of which uranium-235 was concentrated in the aqueous solution, and uranium-238 was distributed as the chelate complex into the organic solvent. Cupferron was recommended to form a chelate complex of uranium(IV): uranium cupferronate is insoluble in water, but soluble in many organic solvents. The most effective solvent was chloroform, which ensured rapid phase separation. Since isotopic fractionation requires many stages, countercurrent contact between organic and aqueous phases, as is usual in continuous countercurrent extraction, was tested and proposed. During the isotopic fractionation the uranium transferable by the organic phases passes successively from stage to stage in one direction, while the uranium-containing aqueous solution passes in the opposite direction. An aqueous solution enriched with uranium-235 was withdrawn at one end of the apparatus, and an organic solution enriched with uranium-238 at the opposite end.

It was proposed also to accomplish isotopic fractionation by countercurrent contact between solutions passing through a vertical packed column. A glass helix-filled 9-m column of diameter 1 cm was used, the aqueous solution flowed upwards, and the organic solution downwards. Clewett et al.[8] considered that the exchange reaction

$$^{238}UCl_{4\,aq} + {}^{235}U[C_6H_5N(NO)O]_4 \rightleftarrows {}^{235}UCl_{4\,aq} + {}^{238}U[C_6H_5N(NO)O]_4 \quad (1)$$

accomplished in this way might lead to a single-stage separation factor of 1.002.

A brief communication by Spedding and Powell[10] also indicated the possibility of achieving this separation factor. Uranium isotopes were separated in a uranyl solution together with a cation-exchange resin. The uranium band was eluted through a column filled with the copper form of Dowex 50 × 8 sulphonated cation-exchange resin (50–100 mesh) by means of 0.005 M aqueous diammonium magnesium ethylenediaminetetra-acetate. The isotopic exchange is described by the equation

$$^{238}UO_{2\,aq}^{2+} + {}^{235}UO_2R \rightleftarrows {}^{238}UO_2R + {}^{235}UO_{2\,aq}^{2+}, \quad (2)$$

where UO_2R and UO_2^{2+} denote uranyl ions in the exchanger and in the aqueous solution respectively. With a band 28 cm long traversing a distance of 90 cm isotopic changes of 4–5% were reported[10] at both ends of the band, enrichment with uranium-235 being observed in the leading portion of the band.

The results obtained by the above workers on the extraction and ion-exchange separation of uranium isotopes led them to make extremely optimistic forecasts of large-scale enrichment. However, it was reported later[11] that attempts to use the extraction method for separating uranium isotopes had been unsuccessful, since cupferron oxidised rapidly, and the resulting oxidation products prevented normal functioning of the countercurrent column.

Finally in 1969 Rutenberg and Drury[12] refuted the above results. They used new equipment to make accurate measurements of isotopic changes in the system formed by a chloroform solution of uranium cupferronate and an aqueous hydrochloric-acid solution in the uranium band of the above experiment by Spedding and Powell. The single-stage separation factor was found to be far lower than the published value (1.002) in both extraction and ion-exchange systems, respectively 1.00007 ± 0.00001 and 1.00006 ± 0.00005. Calculations showed that the above processes for separating uranium isotopes were unacceptable both technically and economically.

The separation of uranium isotopes by chemical methods has been widely investigated in Japan, where attention has been concentrated on the use of ion-exchange resins. A joint paper on this problem was presented by Kakihana et al.[13] at the Third International Conference on the Peaceful Uses of Atomic Energy held in Geneva in 1964. A brief account was given of the theory of the separation of uranium isotopes by isotopic exchange, together with experimental results for an exchanger in a solution of uranium in aqueous hydrochloric acid.

In March 1970 the Japanese newspaper *Asahi Shimbun*[14] published a report on the Annual Symposium of Japanese Nuclear Scientists containing experimental results on the enrichment of uranium by chemical methods. An ion-exchange column of height 1 m and cross-section 1 cm^2 was used with Amberlite IRA-120B, a sulphonated cation-exchange resin. A single passage of an acid sulphate solution of uranium increased the uranium-235 content by 1.017%; fractions of the enriched uranium solution were withdrawn first from the column. On the basis of these results it is planned to set up a new experimental plant 10–30 times as powerful. Several advantages of the new process are emphasised: (*a*) the technical equipment is considerably simpler; (*b*) use of the aggressive and toxic uranium hexafluoride is avoided; and (*c*) Japanese experts estimate that the capital cost of constructing an industrial plant to produce 1000 tonnes of 3% uranium-235 annually will be less than 10% of the cost of constructing a gas-diffusion plant.

A news item[15] referred to Japanese reports of similar work in France.

III. SEPARATION OF URANIUM ISOTOPES BY ION EXCHANGE

The first experiments on the separation of stable isotopes by ion exchange were made more than thirty years ago by Taylor and Urey[16,17]. Since then many investigations have been made on the separation of lithium, boron, sodium, calcium, and nitrogen isotopes on a sulphonated cation-exchange resin in an aqueous electrolyte

solution. However, low separation factors were obtained except in work[18] on the ion-exchange separation of the isotopes of nitrogen. Experiments on uranium isotopes[19] gave separation factors <1.001. Kakihana et al.[20] explained such results by the almost identical states of the isotopes in the external aqueous solution and in the sulphonated cation-exchange resin: systems in which the isotopes are in different chemical states in the phases must be chosen to obtain higher values.

Japanese work on the chemical separation of uranium isotopes has been based on Kakihana and Kurisu's theory of separation by isotopic exchange between uranium(IV) and uranium(VI). These workers made detailed theoretical investigations on the factors on which the efficiency of separation of the isotopes depends[21,22], and deduced the main equation for the separation factors.

Theoretical and experimental investigations published hitherto are surveyed below.

1. ISOTOPIC EXCHANGE IN VARIOUS CHEMICAL SYSTEMS

(*a*) General Principles

Isotopic exchange can be effected by the transfer of isotopic atoms and of electrons. An example of the former is exchange in complex compounds. The first studies on this problem were made by Grinberg and Filinov[23,24]. Numerous subsequent investigations have established that the rate of isotopic exchange in complexes is greatly influenced by such factors as the nature of the ligand[25,26], the sign of the ionic charges[27], the coordination number[28,29], etc.

Isotopic exchange by the transfer of electrons takes place in redox systems. Reactions of this type involve essentially not the exchange of isotopes but a change in their valency states. For example, the exchange of iron between $FeCl_2$ and $*FeCl_3$

$$Fe^{3+} + {}^{*}Fe^{3+} \rightleftarrows Fe^{3+} + {}^{*}Fe^{2+} \qquad (3)$$

can be regarded as the result of two processes leading to electron transfer from Fe^{2+} to $*Fe^{3+}$:

$$Fe^{3+} \rightleftarrows Fe^{3+} + \bar{e} \quad \text{(conversion of unlabelled } Fe^{II} \text{ into } Fe^{III}) \qquad (4)$$

$${}^{*}Fe^{3+} + \bar{e} \rightleftarrows {}^{*}Fe^{2+} \quad \text{(conversion of labelled } Fe^{III} \text{ into } Fe^{II}) \; . \qquad (5)$$

In reality the two stages are not separate, and the electron passes directly from one ion to the other[30]. Such exchange reactions, observed in reversible redox systems, occur at different rates. The rate of exchange is strongly dependent on concentration, acidity, additions of foreign ions, etc.[30]

Investigations on isotopic exchange between uranium(IV) and uranium(VI) in various systems is of great value in connection with the problem of separating uranium isotopes by chemical methods.

(*b*) Hydrochloric-acid Solutions

Detailed investigations of the kinetics and the mechanism of isotopic exchange between uranium(IV) and uranium(VI) were made by Rona[31], who studied the reaction

$$U^{IV} + {}^{*}U^{VI} \rightleftarrows {}^{*}U^{IV} + U^{VI} \; , \qquad (6)$$

where the asterisk denotes the radioactive uranium-233 isotope. The experiments showed that the order of the rate of exchange with respect to the hydrogen-ion concentration was ~3. Rona showed also that the rate of exchange was independent of the addition of neutral salts, the concentration of chloride ions, and illumination. According to Woodward[6], however, light accelerates the reaction considerably (both workers used the light from a tungsten lamp).

In order to understand the mechanism of the above exchange reactions it is important to know the ionic forms of uranium(IV) and uranium(VI). There is weighty evidence that uranium(VI) is present as UO_2^{2+} in moderate acid concentrations[32]. Quadrivalent uranium is assumed to exist as the equilibrium mixture

$$U^{4+} \rightleftarrows U(OH)^{3+} \rightleftarrows U(OH)_2^{2+} \rightleftarrows U(OH)_3^{+} \; . \qquad (7)$$

Rona suggests[31] that, in the uranium(IV–VI) exchange system, the last form $U(OH)_3^+$ will react readily with the uranyl ion to form a complex containing an oxygen bridge between the two ions:

$$U(OH)_3^+ + UO_2^{2+} \underset{\longleftarrow}{\overset{2H_2O}{\rightleftarrows}} Z^{3+} + 2H^+ \; , \qquad (8)$$

where Z^{3+} is a hypothetical intermediate ion, which may have the structure

$$\left[\begin{array}{c} O{=}U{-}O{-}U{-}OH \\ \quad | \quad\quad | \\ \quad OH \quad\; OH \end{array}\right]^{3+} \; .$$

This leads to the possible reaction mechanism of isotopic exchange

$${}^{235}U(OH)_3^+ + {}^{238}UO_2^{2+} \rightleftarrows {}^{235}UO_2^{2+} + {}^{238}U(OH)_3^+ \qquad (9)$$

in which Z^{3+} is the intermediate activated complex taking part in the electron transfer

$$\left[\begin{array}{c} HO{-}{}^{235}U^{IV}{-}OH \\ \quad | \\ \quad OH \end{array}\right]^{+} + \left[\begin{array}{c} {}^{238}U^{VI}{=}O \\ \quad \| \\ \quad O \end{array}\right]^{2+} \rightleftarrows \left[\begin{array}{c} O{=}{}^{235}U{-}O{-}{}^{238}U{-}OH \\ \quad\; | \quad\quad\quad | \\ \quad\; OH \quad\quad\; OH \end{array}\right]^{3+} \rightleftarrows$$

$$\rightleftarrows \left[\begin{array}{c} {}^{235}U^{VI}{=}O \\ \quad \| \\ \quad O \end{array}\right]^{2+} + \left[\begin{array}{c} HO{-}{}^{238}U^{IV}{-}OH \\ \quad\; | \\ \quad\; OH \end{array}\right]^{+} \; . \qquad (10)$$

This isotopic exchange appears to be an exchange of ligands between uranium(IV) and uranium(VI) ions.

The effect of the concentration of hydrochloric acid on the rate of exchange was studied also by Kakihana et al.[33,34], who investigated the homogeneous exchange between natural uranium(IV) and impoverished uranium(VI) in various acid concentrations at 30, 50, and 70°C.

(*c*) Sulphuric-acid Solutions

Studies of the exchange between uranium(IV) and uranium(VI) in aqueous sulphuric acid were described by Betts[35] in 1948. This exchange occurs essentially between the sulphate complexes, in whose inner sphere sulphate ions are assumed to be accompanied by water molecules. The presence of the latter in the inner sphere, and especially of hydroxide ions, both in hydrochloric-acid and in sulphuric-acid solutions as assumed by Grinberg and Bykhovskii[36], facilitates the transition from U^{4+} to UO_2^{2+}.

Baechmann and Lieser[37] found that, in solutions containing sulphate ions in the dark, the rate of electron exchange between uranium(IV) and uranium(VI) is proportional to their concentrations and inversely proportional to the cube of the hydrogen-ion concentration. The reaction velocity is governed by the stage of disproportionation

of uranium(V), present in small quantities in equilibrium with uranium(IV) and uranium(VI). This conclusion was based on Betts' finding[35] that the rate of electron transfer between the latter valency states in sulphate solutions was far greater, and on Heal and Thomas's discovery[38] of higher uranium(V) concentrations, under illumination. The mechanism of electron transfer is represented by

$$U^{4+} + {}^{*}U^{6+} \rightleftarrows U^{5+} + {}^{*}U^{5+} \quad . \tag{11}$$

Subsequent disproportionation of U^{5+} yields $*U^{4+}$:

$$U^{5+} + {}^{*}U^{5+} \rightleftarrows U^{6+} + {}^{*}U^{4+} \quad . \tag{12}$$

Electron exchange between uranium(IV) and uranium(VI) has been investigated also in several other solutions—oxalate[36], perchlorate[39], and aqueous organic[40-43].

(*d*) Cation-exchange Resin in Hydrochloric-acid Solution

Isotopic exchange in a system comprising a cation-exchange resin in a hydrochloric-acid solution was studied by Shimokawa and Nishio[44]. Granules of Dowex 50 × 4 containing ions of impoverished uranium(IV) were placed in a solution of natural uranium(VI). At the start of the reaction a certain quantity of uranium(VI) ions passed into the resin from the solution, but all the uranium(IV) ions remained in the resin throughout the reaction with aqueous acid concentrations up to 1 *N*. Change in the relative content of the uranium(IV) isotope in the resin was followed mass-spectrometrically. Analysis of the system revealed two possible modes of exchange (on the basis that the reaction was bimolecular[45-47]).

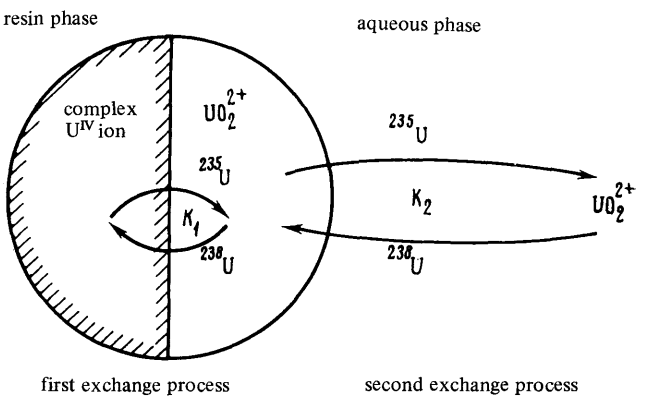


Figure 1. Diagram of two exchange processes.

1. First exchange process. With isotopic exchange between uranium(IV) and uranium(VI) occurring in the resin phase

$$^{235}U^{IV}_{res} + {}^{238}U^{VI}_{res} \overset{K_1}{\rightleftarrows} {}^{238}U^{IV}_{res} + {}^{235}U^{VI}_{res} \tag{13}$$

the isotopic exchange equilibrium constant $K_1 = 1.0007$ (i.e. $1/K_1 = 0.9993$). The fact that K_1 exceeds unity implies that sexivalent uranium is enriched with the 235 isotope when chemical equilibrium is established, and the quadrivalent state with uranium-238.

2. Second exchange process. Isotopic exchange between sexivalent uranium in the resin and sexivalent uranium in solution

$$^{235}U^{VI}_{res} + {}^{238}U^{VI}_{soln} \overset{K_2}{\rightleftarrows} {}^{238}U^{VI}_{res} + {}^{235}U^{VI}_{soln} \tag{14}$$

gives an equilibrium constant $K_2 = 1$. Reaction (13) is more rapid than reaction (14).

Thus isotopic exchange in a system comprising a solution and a cation-exchange resin is represented by the scheme

$$^{235}U^{IV}_{res} + {}^{238}U^{VI}_{soln} \overset{K}{\rightleftarrows} {}^{238}U^{IV}_{res} + {}^{235}U^{VI}_{soln} \quad , \tag{15}$$

whence the equilibrium constant $K = K_1K_2 = 1 + \epsilon$ or

$$K = \frac{^{238}U^{IV}_{res}}{^{235}U^{IV}_{res}} : \frac{^{238}U^{VI}_{soln}}{^{235}U^{VI}_{soln}} . \tag{16}$$

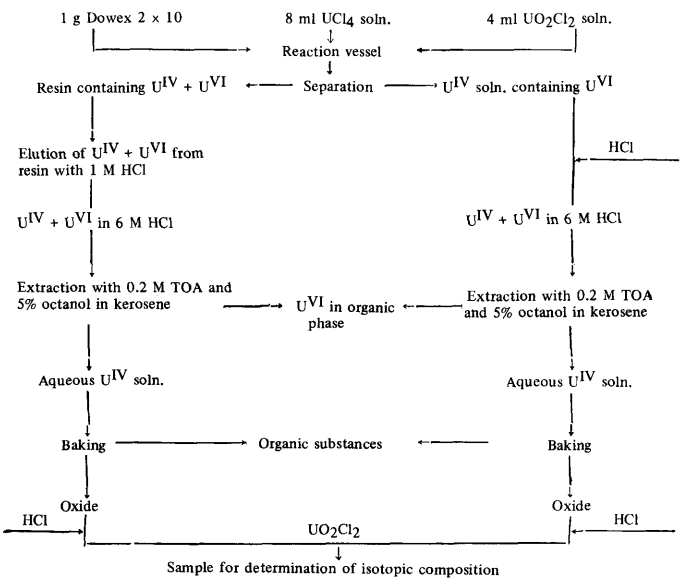
Fig. 1 illustrates diagrammatically the two exchange processes. It follows from Eqn. (15) that uranium-235 is concentrated in the uranium(VI) solution. The rate constant of isotopic exchange was greater in the resin phase than in solution by $\sim 10^3$–10^4, which indicates that the cation-exchange resin catalyses the isotopic exchange of uranium(IV) and uranium(VI).

(*e*) Anion-exchange Resin in Hydrochloric-acid Solution

The first results for the isotopic exchange of uranium(IV) and uranium(VI) in an anion-exchange resin in aqueous hydrochloric acid were presented at the Third International Conference on the Peaceful Uses of Atomic Energy[13]. The experimental procedure (Scheme 1) involved treating samples of Dowex 2 × 8 with 8 M hydrochloric acid containing natural uranium(IV) and impoverished uranium(VI); after ion-exchange equilibrium had been established, the change in the relative content of uranium-235 was monitored at intervals, both for uranium(IV) in the resin and for uranium(VI) in the solution.

Scheme 1.

Study of electron exchange between uranium(IV) and uranium(VI) in a hydrochloric-acid solution impregnating an anion-exchange resin.



The experimental results showed that quadrivalent uranium is enriched with the 235 isotope, and sexivalent uranium with the 238 isotope. Isotopic exchange can occur in three possible ways:

$$^{238}\overline{U}^{IV} + {}^{235}\overline{U}^{VI} \overset{k_1}{\rightleftarrows} {}^{238}\overline{U}^{VI} + {}^{235}\overline{U}^{IV} \quad , \tag{17}$$

$$^{238}U^{IV} + {}^{235}\overline{U}^{IV} \overset{k_2}{\rightleftarrows} {}^{235}U^{IV} + {}^{238}\overline{U}^{IV} \quad , \tag{18}$$

$$^{235}\overline{U}^{VI} + {}^{238}U^{IV} \overset{k_3}{\rightleftarrows} {}^{235}U^{IV} + {}^{238}\overline{U}^{VI} \quad , \tag{19}$$

$$\frac{d[^{235}\overline{U}^{IV}]}{dt} = k_1\{[^{235}\overline{U}^{VI}][^{238}\overline{U}^{IV}] - [^{235}\overline{U}^{IV}][^{238}\overline{U}^{VI}]\} + k_2\{[^{238}U^{IV}][^{238}\overline{U}^{IV}] - [^{235}\overline{U}^{IV}][^{238}U^{IV}]\} \quad , \tag{20}$$

$$\frac{d[^{235}U^{IV}]}{dt} = k_2\{[^{235}\overline{U}^{IV}][^{238}U^{IV}] - [^{235}U^{IV}][^{238}\overline{U}^{IV}]\} + k_3\{[^{235}\overline{U}^{VI}][^{238}U^{IV}] - [^{238}\overline{U}^{VI}][^{235}U^{IV}]\} \quad , \tag{21}$$

$$\frac{d[^{235}\overline{X}^{VI}]}{dt} = k_1\{[^{235}\overline{U}^{IV}][^{238}\overline{U}^{VI}] - [^{235}\overline{U}^{VI}][^{238}\overline{U}^{IV}]\} + k_3\{[^{235}U^{IV}][^{238}\overline{U}^{VI}] - [^{235}\overline{U}^{VI}][^{238}U^{IV}]\} \quad , \tag{22}$$

where [U] and $[\overline{U}]$ represent uranium concentrations in solution and in the resin phase respectively. For simplicity we introduce the notation

$$[^{235}U^{IV}] + [^{238}U^{IV}] = a \qquad [^{235}U^{IV}] = af^{IV}$$
$$[^{235}\overline{U}^{IV}] + [^{238}\overline{U}^{IV}] = \overline{a} \qquad [^{235}\overline{U}^{IV}] = \overline{a}\overline{f}^{IV}$$
$$[^{235}\overline{U}^{VI}] + [^{238}\overline{U}^{VI}] = \overline{b} \qquad [^{235}\overline{U}^{VI}] = \overline{b}\overline{f}^{VI}$$

for the uranium concentrations and the isotopic fractions. During exchange a, $\overline{a}$, and $\overline{b}$ remain constant, while f^{IV}, $\overline{f}^{IV}$, and $\overline{f}^{VI}$ change. Formulae (20)–(22) become

$$\frac{1}{a\overline{b}} \cdot \frac{d\overline{f}^{IV}}{dt} = \frac{1}{a}\{\overline{f}^{VI} - \overline{f}^{IV}\}k_1 + \frac{1}{\overline{b}}\{f^{IV} - \overline{f}^{IV}\}k_2 \quad , \tag{20'}$$

$$\frac{1}{\overline{a}\overline{b}} \cdot \frac{df^{IV}}{dt} = \frac{1}{\overline{a}}\{\overline{f}^{VI} - f^{IV}\}k_3 + \frac{1}{\overline{b}}\{\overline{f}^{IV} - f^{IV}\}k_2 \quad , \tag{21'}$$

$$\frac{1}{a\overline{a}} \cdot \frac{d\overline{f}^{VI}}{dt} = \frac{1}{a}\{\overline{f}^{IV} - \overline{f}^{VI}\}k_1 + \frac{1}{\overline{a}}\{f^{IV} - \overline{f}^{VI}\}k_3 \quad . \tag{22'}$$

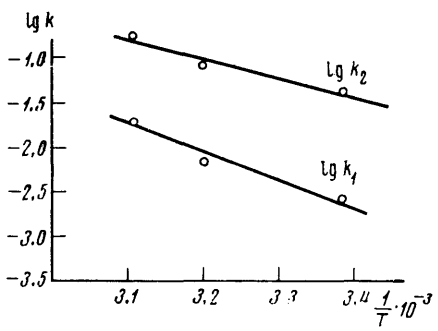


Figure 2. Temperature dependence of reaction rate constant.

The rate constants k_1, k_2, and k_3 can be calculated from Eqns. (20)–(22) by analysing the isotopic composition of samples f^{IV}, $\overline{f}^{IV}$, and $\overline{f}^{VI}$. The apparent reaction rate constant at 30°C was found to be $k_1 = 7.5 \times 10^{-4}$ M^{-1} min^{-1}, which was small in comparison with the value of 3500 [$?3.5 \times 10^{-3}$] M^{-1} min^{-1} in 8 M hydrochloric acid at this temperature. A possible explanation is that the resin phase contains less hydrochloric acid to accelerate this electron exchange[34] than does the acid solution, and that the exchangeable ions do not diffuse so easily in the resin as in the aqueous acid, owing to the effect of functional groups in the anion exchanger.

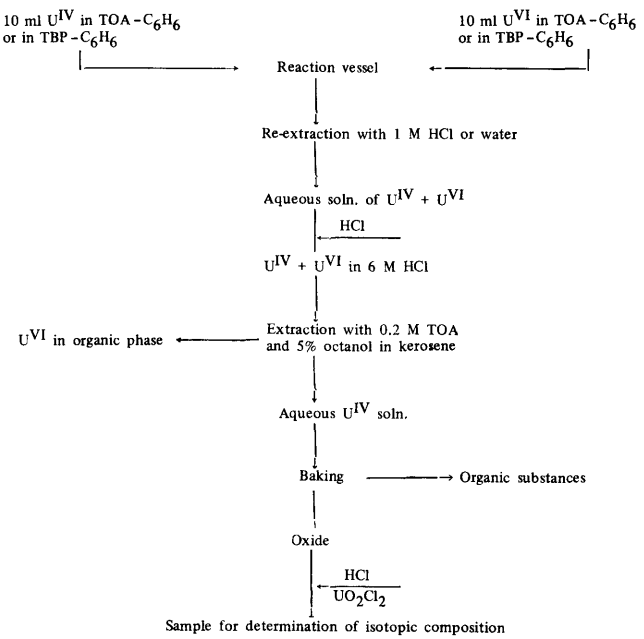
The temperature dependence of the logarithm of the rate constant is plotted in Fig. 2. The activation energy of the electron exchange between uranium(IV) and uranium(VI) in the anion-exchange resin was 22.9 kcal $mole^{-1}$. The closeness of this value to 24–25 kcal $mole^{-1}$ indicates similarity between the activated complexes of this electron exchange in the resin and in 6–10 M hydrochloric acid.

(*f*) Benzene Solution of Trioctylamine (TOA) and Tributyl Phosphate (TBP)

According to Gonda et al. benzene solutions of trioctylamine and tributyl phosphate are extremely promising media for electron exchange between uranium(IV) and uranium(VI).[48] The experimental procedure (Scheme 2) involves mixing equal volumes of benzene solutions of trioctylamine containing respectively natural uranium(IV) and impoverished uranium(VI); a similar operation was made with benzene solutions of tributyl phosphate. In both cases uranium(IV) is enriched with the heavier isotope, and uranium(VI) with the lighter isotope.

Scheme 2.

Study of U^{IV}–U^{VI} electron exchange in TOA–C_6H_6 and TBP–C_6H_6 systems.



The extent of exchange F was determined by means of the equation

$$F = \{f^{IV} - f_0^{IV}\} \cdot \{f_\infty^{IV} - f_0^{IV}\}^{-1} \quad , \tag{23}$$

where f_0^{IV}, f^{IV}, and f_∞^{IV} are the contents of the 235 isotope in uranium(IV) initially, after time t, and finally. The relation between F, the rate of exchange R, and the rate constant k is

$$\ln(1-F) = \ln\{f^{IV} - f_\infty^{IV}\} \cdot \{f_0^{IV} - f_\infty^{IV}\}^{-1} = -R\{[U^{IV}] + [U^{VI}]\} \cdot \{[U^{VI}] \cdot [U^{IV}]\}^{-1}t = -k\{[U^{IV}] + [U^{VI}]\}^{-1}t \quad . \tag{24}$$

The dependence of $\ln(1-F)$ on time is represented by a straight line, from whose slope we can determine R and k.

Rate of exchange increases with decrease in the concentration of trioctylamine or tributyl phosphate in benzene. The explanation is that the complexes of these solutes that are capable of exchange diffuse more easily into dilute than into concentrated solutions. In particular, true rate constants can be determined by measuring exchange in dilute solutions of trioctylamine and tributyl phosphate. The mechanism of exchange when the complex ions are extracted into a benzene solution of trioctylamine is similar to that in an anion-exchange resin.

2. SEPARATION OF URANIUM ISOTOPES IN AN EXCHANGER–SOLUTION SYSTEM CONTAINING URANIUM(IV) AND URANIUM(VI)

(*a*) Separation Factor of Uranium Isotopes

Since isotopic effects in chemical systems met in practice usually balance out, it proved impossible for a long time to obtain for uranium isotopes any appreciable separation factors defining the efficiency of particular systems. Experimental studies made in Japan with the aim of obtaining high separation factors for these isotopes were based on theoretical investigations by Kakihana and Kurisu[21,22,49,50], Ishida[51,52], and Shimokawa[44,53].

The separation factor for uranium isotopes can in general be expressed by the formula

$$^{235}_{238}S = \frac{[^{235}\overline{U}]}{[^{238}\overline{U}]} \cdot \frac{[^{238}U]}{[^{235}U]} = \frac{\Sigma[^{238}U^{IV}]+\Sigma[^{238}U^{VI}]}{\Sigma[^{235}U^{IV}]+\Sigma[^{235}U^{VI}]} \cdot \frac{\Sigma[^{235}\overline{U}^{IV}]+\Sigma[^{235}\overline{U}^{VI}]}{\Sigma[^{238}\overline{U}^{IV}]+\Sigma[^{238}\overline{U}^{VI}]}, \quad (25)$$

where $^{238}U/^{235}U$ is the molar ratio of the isotopes in solution, and $^{235}\overline{U}/^{238}\overline{U}$ the corresponding ratio in the ion exchanger. For a system containing only U^{4+} ions the separation factor is

$$S_1 = \frac{\Sigma[^{238}U^{IV}]}{\Sigma[^{235}U^{IV}]} \cdot \frac{\Sigma[^{235}\overline{U}^{IV}]}{\Sigma[^{238}\overline{U}^{IV}]} . \quad (26)$$

When only uranyl ions UO_2^{2+} are present, we have

$$S_2 = \frac{\Sigma[^{238}U^{VI}]}{\Sigma[^{235}U^{VI}]} \cdot \frac{\Sigma[^{235}\overline{U}^{VI}]}{\Sigma[^{238}\overline{U}^{VI}]} . \quad (27)$$

The electron exchange in solution can be written

$$^{235}U^{VI} + {}^{238}U^{IV} \rightleftarrows {}^{238}U^{VI} + {}^{235}U^{IV} \quad (28)$$

and that in the ion-exchange resin is represented by

$$^{235}\overline{U}^{VI} + {}^{238}\overline{U}^{IV} \rightleftarrows {}^{238}\overline{U}^{VI} + {}^{235}\overline{U}^{IV} . \quad (29)$$

The equilibrium constants of these electron exchanges are—for the solution

$$K_e = \frac{\Sigma[^{238}U^{VI}]}{\Sigma[^{235}U^{VI}]} \cdot \frac{\Sigma[^{235}U^{IV}]}{\Sigma[^{238}U^{IV}]} \quad (30)$$

and for the ion exchanger

$$\overline{K}_e = \frac{\Sigma[^{238}\overline{U}^{VI}]}{\Sigma[^{235}\overline{U}^{VI}]} \cdot \frac{\Sigma[^{235}\overline{U}^{IV}]}{\Sigma[^{238}\overline{U}^{IV}]} . \quad (31)$$

From (26), (27), (30), and (31) we obtain

$$\overline{K}_e = K_e \frac{S_1}{S_2} . \quad (32)$$

Mathematical rearrangement yields

$$^{235}_{238}S = S_2\left(\frac{S_1K_eS_2^{-1}+\bar{\rho}}{1+\bar{\rho}}\right)\left(\frac{K_e^{-1}+\rho}{1+\rho}\right) , \quad (33)$$

where $\rho = \Sigma[U^{VI}]/\Sigma[U^{IV}]$ and $\bar{p} = \Sigma[\overline{U}^{VI}]/\Sigma[\overline{U}^{IV}]$ are the molar ratios of uranium(VI) and uranium(IV) in the solution and in the ion exchanger respectively. Taking logarithms and rearranging slightly, we convert (33) into

$$\ln^{235}_{238}S = \ln S_2 + \ln\left(1+\frac{S_1K_eS_2^{-1}-1}{1+\bar{\rho}}\right) + \ln\left(1+\frac{K_e^{-1}-1}{1+\rho}\right) , \quad (34)$$

which is the fundamental equation for the separation of uranium isotopes in a mixture of uranium(IV) and uranium(VI).

In view of Eqn. (32) we can write (34) in the form

$$\ln^{235}_{238}S = \ln S_2 + \ln\left(1+\frac{\overline{K}_e-1}{1+\bar{\rho}}\right) + \ln\left(1+\frac{K_e^{-1}-1}{1+\rho}\right) , \quad (35)$$

which emphasises the important fact that the greater the difference between ρ and $\bar{\rho}$ the greater the contribution made by K_e to the separation factor. Uranium(IV) is adsorbed preferentially by a cation-exchange resin, and uranium(VI) by an anion-exchange resin. Consequently either resin may be a good secondary phase giving a high separation factor provided that electron exchange (which takes place very slowly in an ordinary aqueous solution) is accelerated by some catalyst, in particular by the resin itself.

(*b*) Separation of Uranium Isotopes by Means of a Cation-exchange Resin

Kakihana et al.[20,54] used frontal analysis to determine separation factors for a sulphonated cation-exchange resin in a hydrochloric-acid solution containing uranium(IV) and uranium(VI). Acid (0.6 M and 2 M) solutions of uranium were passed at 30 ml h^{-1} through a column (of height 100 cm and diameter 1 cm) filled with Dowex 50 × 12 in the hydrogen form (100–200 mesh). Since the experiments were made under non-equilibrium conditions, the separation factor was calculated by means of the approximate formula

$$^{235}_{238}S = 1 + \frac{D}{Q} \cdot \frac{1}{R_0} \quad (36)$$

in which

$$D = \Sigma d = \Sigma \Delta m \cdot \Delta R \quad (37)$$

is the total change in the uranium-235 content of the exchanger, Δm being the absolute uranium content of the sample, $\Delta R = R_0 - R$, where R_0 and R are the uranium-235 contents in the initial solution and in the samples of eluate, and Q is the total quantity of uranium sorbed by the exchanger. The greatest impoverishment with respect to uranium-235 was observed in the early samples containing uranium(IV), and slight impoverishment in samples containing uranyl ions. The reason is that the light isotope is more strongly retained than uranium-238 in the cation-exchange resin. The single-stage separation factor in these experiments was 1.00028–1.00048.

In July 1968 some Japanese workers patented a counter-current method for enriching uranium isotopes by ion exchange, in which electron exchange was effected between uranium(IV) and uranium(VI) in a sulphonated cation-exchange resin in aqueous hydrochloric acid[55]. A solution of uranium(VI) in 1.0 *N* hydrochloric acid flowed upwards into a column in contact with cation-exchange resin granules saturated with uranium(IV), when a certain quantity of uranium(VI) ions remained in the resin. After equilibrium had been established in this counterflow contact, the concentration of uranium-235 in the uranium(VI) solution

had increased by a factor of 1.00035 (the initial concentration was arbitrarily taken to be unity), while its concentration in the uranium(IV) sorbed on the exchanger had decreased by a factor 1/1.00035 = 0.99964. Thus the isotopic exchange constant was

$$K = \frac{^{235}U^{VI}_{soln}}{^{235}U^{IV}_{res}} = \frac{1.00035}{0.99964} = 1.0007$$

at every stage of exchange. After the first contact the 235-enriched uranium(VI) solution was reduced with zinc dust to the quadrivalent state; the product was sorbed on a fresh portion of exchanger in a special column, from which the uranium(IV)-saturated granules entered the second stage of exchange. This stage increased the concentration of uranium-235(VI) in the solution to 1.00035 × 1.00035 = 1.0007, but the concentration of uranium-235(IV) in the resin remained at 1.00035 × 0.99964 = 1. In the next stage the concentration of uranium-235(VI) in solution increased to 1.0007 × 1.00035 = 1.00105, while that of uranium-235(IV) in the resin was 1.0007 × 0.99964 = 1.00034; and so on. Therefore the concentration of uranium-235(VI) gradually increased in the solution leaving the top of the exchange column. The quadrivalent uranium present in the resin discharged from the bottom of the column was oxidised with 1% aqueous hydrogen peroxide to the sexivalent state; uranium(VI) was eluted with 0.5 *N* hydrochloric acid. Oxidation and elution could be combined into a single stage by applying the oxidant and the desorbing solution simultaneously.

An alternative procedure is to combine oxidation and the maintenance of uranium(VI) in the system in the same apparatus. The uranium(IV)-saturated resin then passes down the column as in the previous case, while the oxidant (1% hydrogen peroxide) flows upwards together with the eluant. As a result the resin is converted into the hydrogen form and is discharged at the bottom of the column, while the desorbed solution of uranium(VI) moves upwards in contact with resin granules saturated with uranium(IV); the accompanying isotopic exchange leads to enrichment with uranium-235 of the solution of uranium(IV) emerging from the upper part of the column.

A cascade enrichment scheme, entailing the use of several ion-exchange columns, was proposed on the basis of the above variants. The uranium(VI) feed solution enters the middle of the ion-exchange column and moves upwards in contact with resin granules saturated with uranium(IV). Part of the solution leaving the top of the column is led to a special apparatus for the reduction of uranium(VI), and the resulting uranium(IV) is used to saturate a fresh portion of resin, which is returned to the ion-exchange apparatus and moves downwards, meeting the uranium(VI) solution obtained by oxidative desorption of the resin at the next stage of the enrichment process. The other part of the solution leaving the top of the column is fed to the next ion-exchange column. Thus each ion-exchange column within the cascade is fed by admitting near its midpoint a portion of the uranium(VI) solution emerging from the top of the ion-exchange column of the preceding stage and a portion of the uranium(VI) solution obtained by oxidative desorption in the next stage. A uranium solution enriched with the heavy isotope is obtained from the bottom of the ion-exchange column at one end of the cascade, and a solution enriched with the light isotope from the top of the column at the other end.

Interesting experiments aimed at intensifying the isotopic effect in a cation-exchange resin immersed in a hydrochloric-acid solution of uranium were made by Shimokawa and Kobayashi[56], who fed iron(III) chloride solution to a column filled with the resin saturated with uranium(IV). The latter underwent oxidation to uranium(VI), after which uranyl ions were eluted from the resin:

$$3\,R_4U^{IV} + 10\,FeCl_3 + 6\,H_2O \rightleftarrows 3\,U^{VI}O_2Cl_2 + 4\,R_3Fe^{III} + 6\,FeCl_2 + 12\,HCl \quad . \qquad (38)$$

The change in valency of the uranium is expressed by the electron exchange

$$U^{IV} + 2\,Fe^{III} \rightleftarrows U^{VI} + 2\,F^{II} \quad . \qquad (39)$$

The UO_2^{2+} and Fe^{2+} ions are rapidly eluted from the column on the arrival of fresh portions of iron(III) chloride, because the affinity of the cations for the resin varies in the sequence

$$Fe^{3+},\ U^{IV} > UO_2^{2+},\ Fe^{2+} > H^+ \quad .$$

The rates of the chemical reactions and of elution are so large that a very sharp band is formed between the iron(III) and uranium(IV) forms of the exchanger. This band moves at a constant speed determined by the quantity of uranium(IV) sorbed initially and by the concentration and the rate of supply of iron(III) chloride. The process is shown diagrammatically in Fig. 3. During the initial period of operation of the column some of the eluted uranyl ions penetrate the uranium(IV) form of the resin and exchange with hydrogen ions of the latter. After the equilibrium partition of uranyl ions between resin and solution has been established, the concentration of uranyl ions in the eluate becomes constant: uranium(IV) is firmly retained in the band.

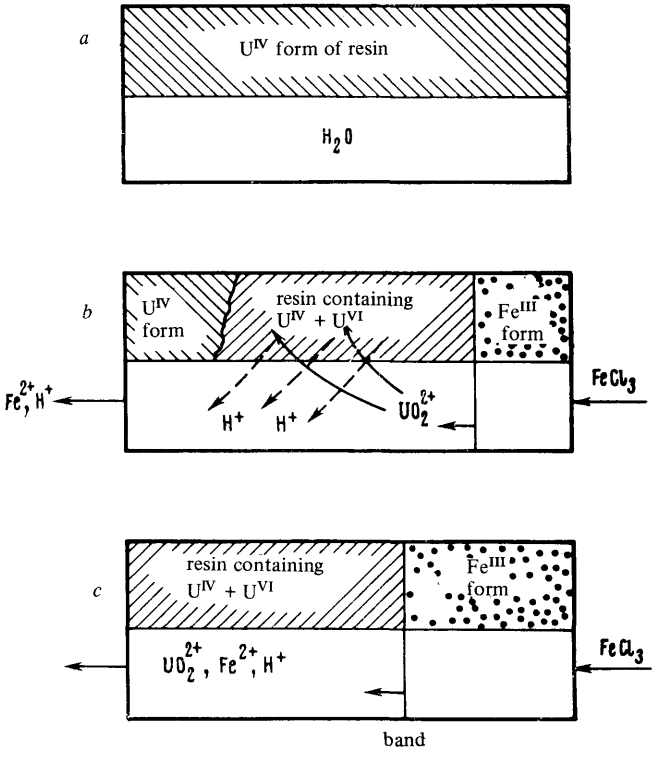


Figure 3. Diagram of movement of band: *a*) before supply of solution; *b*) during initial period of operation of column; *c*) after equilibrium distribution of UO_2^{2+} has been established.

These workers[56] reckoned on strengthening the isotopic effect firstly by the chemical reactions occurring as the band moved along the column and secondly by electron exchange between the two valency states of uranium. The equilibrium constant of isotopic exchange in these experiments was 1.0004–1.0006, regarded as relatively high. It had been reported[57] that such an equilibrium constant should be higher at low temperatures. But the above experiments at 3°C revealed no appreciable fractionating effect; at 20 and 40°C the equilibrium constant of isotopic exchange was respectively 1.0005 and 1.0006.

(*c*) Separation of Uranium Isotopes by Means of an Anion-exchange Resin

Kakihana et al.[58] used Dowex 2 × 10 (100–200 mesh) in the chloride form, in a column of height 100 cm and diameter 1.2 cm, together with solutions in concentrated (8 *N*) hydrochloric acid containing uranium(IV), uranium(VI), and a mixture thereof, flowing at 16 ml h^{-1}. Frontal analysis showed that the separation factor of 0.9993 for solutions containing only uranium(IV) was higher than the value for the mixed solutions (0.9992–0.9986), which can be attributed to the strong influence of the electron exchanges described by Eqn. (19). Indeed, all the experimental results agreed well with theoretical values obtained from Eqn. (35) on the assumption that $K_e = 1.002$.

In 1968 Gonda and Kakihana published experimental results on the fractionation of uranium isotopes in an anion-exchange resin immersed in benzene solutions of trioctylamine and tributyl phosphate[59]. Frontal analysis was used to investigate isotopic exchange for four solutions containing natural uranium (0.72% of uranium-235)— (i) 0.05 M solution of trioctylamine in benzene saturated with uranium(IV), (ii) a mixture of 0.05 M solutions of trioctylamine in benzene saturated respectively with uranium(IV) and uranium(VI), (iii) 0.05 M solution of tributyl phosphate in benzene saturated with uranium(IV), and (iv) a mixture of 0.05 M solutions of tributyl phosphate in benzene saturated respectively with uranium(IV) and with uranium(VI). An ion-exchange column of height 100 cm and diameter 1.3 cm was filled with Dowex 21K (50–100 mesh). Solutions were passed through at 25 ml h^{-1} until the uranium solution had the same composition leaving and entering the column.

In the benzene solution of tributyl phosphate saturated with a mixture of uranium(IV) and uranium(VI) the first samples of eluate obtained on determining the elution sorption curve contained uranium enriched with the lighter isotope (0.732%), by a factor of 1.017 relative to the natural content. This indicates that in this system uranium-238 is more readily sorbed than is uranium-235. The single-stage factor for a solution containing a mixture of valency states was 0.99988, and that for a solution containing only quadrivalent uranium was 0.99989.

The first eluate samples obtained for the elution curve in a benzene solution of trioctylamine saturated with the mixture of valency states were impoverished with respect to the lighter isotope (0.710%, by a factor of 0.987). Hence uranium-235 is more easily sorbed than uranium-238 from a benzene solution of trioctylamine; the single-stage separation factor for this system is 1.00033.

The complete absence of any isotopic effect in the trioctylamine–benzene system saturated only with quadrivalent uranium is due to the similarity in the binding of the latter in the anion-exchange resin and in the solution.

From the above mass-spectrometric results and the fact that uranium(VI) exhibits the greater affinity for the anion-exchange resin in the benzene–tributyl phosphate system, whereas quadrivalent uranium has the greater affinity in benzene–trioctylamine solutions, it was concluded that uranium-235 is concentrated in the quadrivalent state. This is consistent with results for an anion exchanger in 8 M hydrochloric acid containing the mixed valency states[58]. The equilibrium constants of electron exchange in 0.05 M solutions of trioctylamine and of tributyl phosphate in benzene are respectively 1.0010 and 1.0013, both smaller than the equilibrium constant (1.002) in 8 M hydrochloric acid.

3. SEPARATION OF URANIUM ISOTOPES ON A CATION-EXCHANGE RESIN IN A URANYL SALT SOLUTION

Ciric and Zmbov[60,61] studied the separation of uranium isotopes during ion exchange on a cation-exchange resin in an aqueous solution of a uranyl salt. The columns used (l = 1–2 m with S = 0.5 or 1.5 cm^2) were filled with Dowex 50 × 8 or Amberlite IR-120 resin (size of granules 100–200 mesh or 0.1–0.2 mm respectively). The enrichment coefficient was determined by frontal analysis with the application of Glueckauf's equation[62]

$$\varepsilon = \frac{\pi\eta^2}{4\bar{v}s'}\left(1+\frac{\pi\eta}{4}+\frac{5\pi^2\eta^2}{64}+\ldots\right), \qquad (40)$$

where $\eta = (N_0 - N)/N_0$ is the relative enrichment of the more strongly adsorbed isotope in the sample, s' is the gradient of relative enrichment in the sample, $\bar{v}$ is the volume of the sample, and $\epsilon = \alpha - 1$, in which α is the separation factor. We can also apply Spedding's equation[18]

$$\varepsilon = \frac{\sum_{i=1}^{m} V_i C_i (N_0 - N_i)}{QN_0(1-N_0)}, \qquad (41)$$

where V_i, C_i, and N_i are respectively volume, concentration, and content of the more strongly adsorbed isotope in the sample, and Q is the quantity of resin (in equivalents) traversed by the front. Experiments were made with solutions of uranyl nitrate, chloride, and sulphate.

Table 1. Experimental determination of separation factor in systems containing various uranyl salts.

Cation exchanger	Column	Solution		α
		uranyl salt	concn., M	
Amberlite IR-120	l=2 m S=0.5 cm^2	$UO_2(NO_3)_2$	0.3	1.00015±0.00005
		$UO_2(NO_3)_2$	1.0	1.00010±0.00005
		$UO_2(NO_3)_2$	2.0	1.00017±0.00005
		$UO_2(NO_3)_2$	4.0	1.00010±0.00005
Dowex 50 × 8	l=1 m S=1.5 cm^2	$UO_2(NO_3)_2$	2.0	1.0005±0.0002
		UO_2Cl_2	1.0	1.0004±0.0001
		UO_2Cl_2	2.0	1.0006±0.0002
		$UO_2(ClO_4)_2$	1.0	1.0006±0.0001
		UO_2SO_4	2.0	1.00004
		UO_2-tartrate	0.2	.00000

The experimental results show (Table 1) that the separation factor $\alpha = (^{238}U/^{235}U)_{soln}/(^{238}U/^{235}U)_{res}$ varies from unity to 1.0006. The effect of the uranyl salt concentration on the separation factor lies within the limits

of experimental error. The isotopic effect obtained with uranyl nitrate, chloride, and perchlorate is due solely to the ion-exchange reaction[53]

$$^{235}UO_{2\,soln}^{2+} + {}^{238}UO_{2\,res}^{2+} \rightleftarrows {}^{238}UO_{2\,soln}^{2+} + {}^{235}UO_{2\,res}^{2+} \quad . \qquad (42)$$

The strongly hydrated heavier isotope concentrates in the solution, and the lighter isotope in the resin. Lower values were obtained for uranyl sulphate and tartrate, owing to the isotopic effect of the reaction

$$^{235}UO_2^{2+} + {}^{238}UO_2A \rightleftarrows {}^{238}UO_2^{2+} + {}^{235}UO_2A \quad , \qquad (43)$$

where A is an anion forming a complex with the uranyl ion, which partly or completely nullifies the isotopic effect of reaction (42).

4. SEPARATION OF URANIUM ISOTOPES BY A MOVING BAND

Ciric and Zmbov[60,61] used a moving band with non-spreading boundaries, often termed also Spedding's method, to increase the separation of uranium isotopes. The method consists essentially in the movement of a band of constant length through a system of interconnected ion-exchange columns. This procedure enabled Spedding et al.[18] to achieve complete separation of macroquantities of nitrogen isotopes.

The uranyl band can be moved in a cation-exchange resin in two ways: (*a*) a solution containing a doubly charged cation having greater affinity for the exchanger than has the uranyl ion is used to advance the uranyl band in a column filled with Dowex 50 × 8 in the hydrogen form (choice of a suitable cation presents no special difficulty[63]); or (*b*) the band is moved by means of solutions of salts of weak acids whose anions form stable uranyl complexes. In the elution of a uranyl band with an ammonium acetate buffer, for example, the desorption equilibrium

$$2(NH_4^+)_{soln} + (HAc)_{soln} + 2(Ac^-)_{soln} + UO_{2\,res}^{2+} \rightleftharpoons 2(NH_4^+)_{res} + ([UO_2Ac_3]^-)_{soln} + (H^+)_{soln} \qquad (44)$$

and the adsorption equilibrium

$$(H^+)_{soln} + [(UO_2Ac_3^-]_{soln} + 2(H^+)_{res} \rightleftharpoons UO_{2\,res}^{2+} + 3(HAc)_{soln} \qquad (45)$$

are displaced considerably to the right in the lower part of a column filled with the resin in the hydrogen form. As a consequence, both edges of the band are very sharp, so that its length remains constant during elution. Ammonium acetate can be replaced by the citrate, glycollate, lactate, or other ammonium salts.

Table 2.

Cation exchanger	α
Amberlite IR-120	1.00016±0.00005
Dowex 50 × 8	1.0004±0.00001

The original experiments were made in columns (1 m × 0.5 cm^2) filled with Amberlite IR-120 or Dowex 50 × 8, with ammonium citrate solution (0.29 M of pH 4.4) as eluant. The length of the band was 4 cm. The separation factor α was determined by means of Glueckauf's[19] and Spedding's[18] equations, and the results are listed in Table 2.

The next experiment used columns (S = 1.5 cm^2) of Dowex 50 × 8 cation-exchange resin connected in series. The band length was 11 cm with the same eluant. The experiment was terminated after the band had travelled 6.5 m at 10 cm h^{-1}. The uranium-235 content changed from 0.670% in the first few samples to 0.740% in the last sample. An experiment using the same eluant with a band length of 54 cm was terminated after a travel of 14 m. Although the system was far from equilibrium, the uranium-235 content in the last sample was 0.760%.

In another case the initial band length was 8 cm (actually 11 cm because of the slope of leading and trailing edges), elution was effected by ammonium citrate (0.25 M of pH 4.95), and the experiment was stopped after the band had travelled 1.5 m at 3 cm h^{-1}. The uranium-235 contents in first and last samples were 0.640 ± 0.010% and 0.744 ± 0.005%, with α = 1.0004 ± 0.0001.

The experiments described above show that Dowex 50 × 8 gives higher values than does Amberlite IR-120.

5. SEPARATION OF ISOTOPES IN AN ION-EXCHANGE COLUMN WITH APPLICATION OF AN ELECTRIC FIELD

In 1950 some Japanese workers were successful in separating copper and nickel isotopes by applying a constant electric field to an ion-exchange resin. Since then repeated attempts have been made to use ion exchangers to separate isotopes of various elements by electromigration[64-69].

Table 3. Enrichment with uranium-235 by electromigration.

Duration of electromigration, h	400	600	1000
Isotopic ^{235}U content in anodic compartment, %	0.709±0.004	0.715±0.004	0.720±0.007
Quantity of ^{235}U remaining in anodic compartment, mg	728	63	4

The effect produced by applying an alternating electric field was described by Japanese scientists in a paper at the Third International Conference on the Peaceful Uses of Atomic Energy[13]. A borosilicate glass vessel was used, divided by cation-exchange membranes into several compartments. One end compartment was filled with ammonium chloride solution to separate the nitrogen isotopes and to serve as anolyte, while the cathode compartment at the other end was filled with aqueous hydrochloric acid; all the intermediate compartments were filled with a cation-exchange resin. Ion-exchange electromigration of ammonium ions was accomplished by applying an alternating current, when the ammonium ion passed through the cation-exchange resin from anode to cathode, changing the direction of its motion with variation in the a.c. phase. The above experiment showed that the heavier isotope nitrogen-15 reaches the cathode compartment more rapidly than does the lighter isotope nitrogen-14.

This method has been used with the same apparatus for the enrichment of uranium-235, whose content in the initial sample of uranyl nitrate was 0.702 ± 0.005%. Amberlite IR-120 of type 2 (in the hydrogen form) was

used, of diameter 2 cm and length 75 cm; the anodic compartment contained 40 ml of 0.5 M uranyl nitrate solution and the cathodic compartment 40 ml of 0.5 M nitric acid. The results are listed in Table 3. This method may give good results[13] in the enrichment of uranium isotopes.

6. Separation of Uranium Isotopes by Electromigration

Cation-exchange membranes are effective for the separation of lithium isotopes[66], and appreciable enrichment has been observed also with uranium. The use of ion-exchange membranes is attractive because the solvation (or hydration) of isotopic ions is far less in them than in solution. This means that the difference in mass between isotopes may have a greater effect on separation in a membrane than in solution. This method has proved most effective for the separation of lithium isotopes in comparison with potassium, copper, and uranium isotopes[70]. The single-stage separation factor for uranium-235 and uranium-238 was 1.00006.

REFERENCES

1. F. S. Patton, D. M. Googin, and W. L. Griffiths, "Nuclear Fuel based on Enriched Uranium" (Translated into Russian), Atomizdat, 1968.
2. A. K. Brewer and S. L. Madorsky, et al., J. Res. Nat. Bur. Stand., 38, 137 (1947).
3. S. L. Madorsky and S. Straus, J. Res. Nat. Bur. Stand., 38, 185 (1947).
4. S. L. Madorsky and S. Straus, J. Res. Nat. Bur. Stand., 41, 41 (1948).
5. A. K. Brewer and S. L. Madorsky, Chem. Abs., 47, 1037a (1953).
6. R. W. Woodward, US P. 2787587 (1957).
7. L. P. Twichell, R. D. Williams, and A. Clark, Nuclear Science Abstracts, 12, 3608 (1958).
8. G. H. Clewett, D. Waine, A. Lee, and W. B. Schaap, US P. 2835687 (1958).
9. G. H. Clewett, Chemical Exchange as a Versatile Isotope Separation Process, 1950.
10. F. H. Spedding and J. E. Powell, USAEC, Report G.S.C. 475 (1954).
11. Nuclear Science Abstracts, 12, 2035 (1958).
12. A. C. Rutenberg and J. S. Drury, J. Inorg. Nuclear Chem., 31, 2289 (1969).
13. H. Kakihana et al., Proceedings of the Third International Conference on the Peaceful Uses of Atomic Energy (Geneva, 1964), United Nations, New York, 1965, P/439.
14. "Asahi Shimbun" (28th March 1970).
15. Chem. Eng., 77, No. 8, 55 (1970).
16. T. Taylor and H. Urey, J. Chem. Phys., 5, 597 (1937).
17. T. Taylor and H. Urey, J. Chem. Phys., 6, 429 (1938).
18. F. H. Spedding and J. E. Powell, J. Amer. Chem. Soc., 77, 6125 (1955).
19. E. Glueckauf et al., Discuss. Faraday Soc., No. 7, 199 (1949).
20. H. Kakihana, J. Chim. phys., 60, 81 (1963).
21. H. Kakihana and K. Kurisu, J. Atomic Energy Soc. Japan, 5, 292 (1965).
22. H. Kakihana and K. Kurisu, Nippon Kagaku Zasshi, 86, 151 (1965).
23. A. A. Grinberg and F. M. Filinov, Dokl. Akad. Nauk SSSR, 23, 918 (1939).
24. A. A. Grinberg and F. M. Filinov, Dokl. Akad. Nauk SSSR, 31, 435 (1941).
25. K. B. Duffield and M. Calvin, J. Amer. Chem. Soc., 68, 557 (1946).
26. J. D. Johnston and N. F. Hall, J. Amer. Chem. Soc., 70, 2344 (1948).
27. F. A. Long, J. Amer. Chem. Soc., 73, 537 (1951).
28. A. W. Adamson et al., J. Amer. Chem. Soc., 724030 (1950); 73, 4786, 5710 (1951).
29. A. G. MacDiarmid and N. F. Hall, J. Amer. Chem. Soc., 76, 4222 (1954).
30. A. M. Brodskii, "Khimiya Izotopov" (Chemistry of Isotopes), Izd. Akad. Nauk SSSR, Moscow, 1957, p. 334.
31. H. Rona, J. Amer. Chem. Soc., 72, 4339 (1950).
32. H. W. Crandall, J. Chem. Phys., 17, 602 (1949).
33. Nuclear Science Abstracts, 20, 14570 (1966).
34. H. Tomiyasu, H. Fukutomi, and H. Kakihana, J. Inorg. Chem., 30, 2501 (1968).
35. H. Betts, Canad. J. Res., 26, 702 (1948).
36. A. A. Grinberg and D. N. Bykhovskii, Radiokhimiya, 4, 234 (1962).
37. K. Baechmann and K. H. Lieser, Nuclear Science Abstracts, 20, 14574 (1966).
38. H. Heal and J. Thomas, Trans. Faraday Soc., 41, 11 (1949).
39. B. Masters and L. Schwarts, J. Amer. Chem. Soc., 83, 2620 (1961).
40. D. M. Mathews, J. D. Hefley, and E. S. Amis, J. Phys. Chem., 63, 1236 (1959).
41. S. L. Melton, J. O. Wear, and E. S. Amis, J. Inorg. Nuclear Chem., 17, 317 (1961).
42. S. L. Melton, A. Jndelli, and E. S. Amis, J. Inorg. Nuclear Chem., 17, 325 (1961).
43. J. O. Wear, J. Inorg. Nuclear Chem., 25, 1445 (1963).
44. J. Shimokawa, G. Nishio, and T. Komori, J. Nuclear Sci. Tech., 1, 2 (1964).
45. D. Cohen, J. C. Sullivan, and J. C. Hindman, J. Amer. Chem. Soc., 77, 4964 (1955).
46. D. Cohen, J. C. Sullivan, and J. C. Hindman, J. Amer. Chem. Soc., 76, 352 (1954).
47. D. Cohen, J. C. Sullivan, and J. C. Hindman, J. Amer. Chem. Soc., 79, 3672 (1956).
48. K. Gonda, H. Kawashima, and H. Kakihana, J. Nuclear Sci. Tech., 5, No. 4 (1968).
49. H. Kakihana and K. Kurisu, Nippon Kagaku Zasshi, 84, 470 (1963).
50. H. Kakihana and K. Kurisu, Nippon Kagaku Zasshi, 84, 16, 784 (1963).
51. K. Ishida, J. Atomic Energy Soc. Japan, 6, 249 (1964).
52. K. Ishida, J. Shimokawa, and Y. Yamomoto, J. Atomic Energy Soc. Japan, 4, 239 (1962).
53. J. Shimokawa and F. Kobayashi, J. Nuclear Sci. Tech., 4, 63 (1967).
54. K. Kakihana, Y. Hori, H. Sato, and T. Kanzaku, J. Atomic Energy Soc. Japan, 4, 857 (1962).
55. B. P. 1120208 (1968).
56. J. Shimokawa and F. Kobayashi, Isotopenpraxis, 1970, No. 5–6, 170.
57. T. Bigeleisen and M. Mayer, J. Chem. Phys., 15, 261 (1947).
58. H. Kakihana et al., J. Atomic Energy Soc. Japan, 5, 990 (1963).
59. K. Gonda and H. Kakihana, Nuclear Sci. Abstracts Japan, 1, 05221 (1968).
60. M. Ciric and F. Zmbov, Abh. Deutsch. Akad. Wiss. Berlin, Kl. Chem. Geol. Biol., 7, 223 (1964).

61. H. Ciric, Energie nucleaire, **10**, 376 (1968).
62. E. Glueckauf et al., Discuss. Faraday Soc., No. 7, 199 (1949).
63. O. Bonner and L. Smith, J. Phys. Chem., **61**, 326 (1957).
64. J. Aoygama et al., J. Atomic Energy Soc. Japan, **4**, 700 (1962).
65. H. Kakihana, Bull. Chem. Soc. Japan, **35**, 2055 (1962).
66. H. Kakihana and M. Okamoto, J. Chem. Soc. Japan, **34**, 402 (1963).
67. H. Kakihana, J. Atomic Energy Soc. Japan, **6**, 65 (1964).
68. H. Kakihana, J. Inorg. Nuclear Chem., **24**, 1145 (1962).
69. H. Kakihana, Proc. 17th Annual Meeting Chem. Soc. Japan, 1964, p. 93.
70. H. Kakihana, M. Okamamoto, and Y. Fuyu, Isotopenpraxis, **4**, 232 (1968).