

the irradiation of zinc with α -particles in a cyclotron and the γ -activity was measured with a scintillation counter having a sodium iodide crystal as scintillator. A gallium nitrate solution of a given pH was mixed with radioactive gallium EDTA or EDTA-OH complex solution of the same pH value and a part of the gallium ion was precipitated with 8-quinolinol at a certain lapse of time. The precipitate was filtered off, with a sintered glass filter plate, washed, dried, weighed and submitted to γ -ray counting.

The result is quite different from that for the corresponding exchange of indium²⁾. The rate is very small in a neutral or an acid solution of pH more than 2, and is very great in a

TABLE. DEPENDENCE OF R UPON VARIOUS FACTORS AND SOME CONSTANTS FOR THE EXCHANGE IN AN AQUEOUS SOLUTION OF pH 7 TO 9

	Ga-EDTA-OH	Ga-EDTA
[OH ⁻]	Proportional	Proportional
[a]	Independent	Independent
[b]	Proportional	Proportional
Ionic strength	Dependent to a less extent	Dependent to a less extent
Concn. of buffer	Almost independent	Almost independent
$k/[OH^-]_{25^\circ C}(\text{sec}^{-1})$	32	12
E_A (kcal./mol.)	27	25
A (sec ⁻¹)	3×10^{15}	2×10^{13}
ΔS (cal./mol./deg.)	+11	+1

At an ionic strength $\mu=0.2$ (KNO₃). A , frequency factor for k ; ΔS , entropy of activation for k on the assumption $\kappa=1$ (κ , transmission coeff.), at pH 8.0.

Isotopic Exchange of Gallium between the Gallium(III) Ion and its Ethylenediamine- N, N, N', N' -tetraacetate and N -2-Hydroxyethylethylenediamine- N, N', N' -triacetate in an Aqueous Solution

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As an extension of the present authors' study of the isotopic exchange of metal chelate compounds having d^{10} structure^{1,2)}, they have examined the kinetics of exchange of gallium between the gallium(III) ion and its ethylenediamine- N, N, N', N' -tetraacetate (EDTA) and N -2-hydroxyethylethylenediamine- N, N', N' -triacetate (EDTA-OH) in water by the use of gallium-67. The radioisotope was produced by

basic medium. In the pH range from 7 to 9, the exchange proceeds at a measurable rate. Since the exchange constant R expressed according to McKay's formula³⁾ is proportional to the concentration of the chelate b and is independent of that of the gallium ion a , the rate constant k is shown as R/b . Dependence of R upon various factors is shown in the Table together with other constants of the reaction. It is rather marked that the energy of activation E_A is very great as compared with that for the exchange of indium in an acid solution (10 kcal. per mol.). The present authors tend to suggest that the attack of the hydroxyl ion upon the central gallium in the co-ordination compound might play an important role in determining the exchange rate. Detail of the result and discussion on the reaction mechanism will be published later.

1) K. Saito and M. Tamura, This Bulletin, 32, 533 (1959).

2) K. Saito and M. Tamura, J. Inorg. Nur. Chem., 13, 334 (1960).

3) H. A. C. McKay, Nature, 142, 997 (1938).

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