THE ISOTOPIC SEPARATION OF OXYGEN, CHLORINE, BROMINE, AND NITROGEN BY THE CHEMICAL METHODS.

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The author has pointed out two effects in the isotopic exchange reactions.[1] According to effect B which the author has considered first, the following theory has been presented; that is, the element is rich in heavier isotope when it is in the more positively polarised state. Effect B will be more important in the isotopic separation of the element by the chemical methods.

The Chemical Separation of Oxygen Isotopes. *The Separation by Sulphuric Acid.*[2] The isotopic shifts of hydrogen and oxygen isotopes due to effect B will be expected in the exchange reaction between hydroxyl radical and hydrated hydrogen ion: $(=O^{16}H^{+}) + (-O^{18}D) = (=O^{18}D^{+}) + (-O^{16}H)$. Two mols of water was added to 1 mol of sulphuric acid, and water was divided into two portions by distillation. Two mols of water of the latter fraction was added to 1 mol of sulphuric acid now used and fractionated into two portions. This treatment was repeated 6 times. The density increase compared with ordinary water was 1.6×10^{-6} after the 2nd treatment, 3.1×10^{-6} after the 4th treatment, and 8.2×10^{-6} after the 6th treatment. When dried CO_2 was passed, the density increase went down to 5.8×10^{-6}. Similarly the density increase went down to 4.9×10^{-6} by dried air. The density decrease due to air can be attributed to the following exchange reaction: $(-O^{18}H) + O^{16}O^{16} = (^{-}O^{16}H) + O^{16}O^{18}$.

The Separation by Sodium Hydroxide. One half of 80 g. of water was converted into hydrogen and NaOH by sodium. In this case the density of water must increase due to effect B. The isotopic shift of hydrogen by the evolution of hydrogen by sodium can be calculated as 3.3×10^{6}, assuming that the separation coefficient in this case is 2. The equilibrium constant of exchange reaction between OH^{-} and $-OH$ is 0.42.[3] The isotopic shift of hydrogen due to this reaction can be calculated as 3.6×10^{-6}. The density increase actually observed was 9.5×10^{-6}. From these results the density

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(2) *Tech. Repts Kyushu Imp. Univ.*, **11** (1936), 1.
(3) This Bulletin, **11** (1936), 425; *Tech. Repts Kyushu Imp. Univ.*, **10** (1935), No. 6.

increase due to O^{18} is calculated as 2.6×10^{-6}. The separation coefficient of oxygen is 1.02.

The Separation by Potassium Nitrate. The density increase of water must be expected to be due to the following exchange reaction: $(=NO^{18-}) + (-O^{16}H) = (=NO^{16-}) + (-O^{18}H)$. The density increase of water of 2.57 mols KNO_3 solution is 1.2×10^{-6}. The equilibrium constant in this case is 1.006.

The Chemical Separation of Chlorine Isotopes.[4] Chlorine is a mixture of Cl^{35} and Cl^{37}. The packing fractions are -4.8 and -5.2, respectively. The abundance ratio is 3.0~3.1 : 1. The chemical atomic weight is 35.457.

In the exchange reaction between chlorine ion hydrate and chlorine molecule, the isotopic shift of Cl^{37} in Cl_2 can be expected to be due to effects A and B.

$$Cl^{37-}_{aq.} + Cl^{35}Cl^{35} = Cl^{35-}_{aq.} + Cl^{35}Cl^{37}\ .$$

HCl was oxidized to Cl_2 with HNO_3 and $KMnO_4$ in the existence of H_2SO_4. The amount of HCl was decreased to 1/9.5 by this process (Table 1, B). Another portion of HCl was decreased to 1/19.7 by converting to Cl_2 with $KMnO_4$ alone in the existence of H_2SO_4 (Table 1, C). HCl was converted to NaCl and the latter recrystallized 3 times. Exactly equal weights of NaCl were taken and each precipitated with accurately the same volume of $AgNO_3$ solution, in slight excess. After precipitation the excess of $AgNO_3$ was determined nephelometrically (Table 1).

Table 1.

	NaCl(g.)	$AgNO_3$(g.)	Atomic weight of Cl
A(Kahlbaum's NaCl, recryst.)	6.0025	17.4463	35.453
,,	6.0025	17.4463	35.453
B	6.0025	17.4506	35.439
C	6.0025	17.4576	35.416

The separation coefficients are 0.980 from the result of B, 0.964 from the result of C.

The Chemical Separation of Bromine Isotopes.[4] Bromine is a mixture of two isotopes Br^{79} and Br^{81}. The packing fractions are -9.0 and -8.6, respectively. The abundance ratio is 1 : 1. The chemical atomic weight is 79.916.

In the exchange reaction between bromine ion hydrate and bromine molecule, the isotopic shift of Br^{81} in bromine can be expected to be due to effect A and B. Bromine (500 g.) in complete solution was converted into Br^-, BrO^-, and BrO_3^- by the action of NaOH, 1/19.2 of the total amount

(4) *Tech. Repts Kyushu Imp. Univ.*, **11** (1936), No. 2.

being left unchanged. The exchange reaction proceeds completely. Bromine was converted into NaBr and recrystallized 3 times and determined in the same way as chlorine (Table 2, B).

Table 2.

	NaBr(g.)	$AgNO_3$(g.)	Atomic weight of Br
A(Merck's NaBr, recryst. 2 times)	5.7077	9.4228	79.911
,,	6.1752	10.1947	79.908
B	5.3249	8.7813	80.023

The separation coefficient is 1.076.

The Chemical Separation of Nitrogen Isotopes. Nitrogen is a mixture of two isotopes of N^{14} and N^{15}. The packing fractions are 6.0 and 2.0. The abundance ratio is 99.86 : 0.14. The chemical atomic weight is 14.008.

In the exchange reaction between ammonium ion and nitrogen molecule:

$$N^{14}H_4^+ + N^{14}N^{15} = N^{15}H_4^+ + N^{14}N^{14},$$

ammonium ion will be rich in N^{14} according to effect A alone, and contrarily rich in N^{15} according to effect B alone.

Ammonium chloride (720 g.) was dissolved in 5 litres of water containing an excess of bromine. Into this solution concentrated NaOH solution was added drop by drop with constant stirring. The amount of NH_4Cl was decreased to 1/3.54 (Table 3, B) and 1/11.26 (C). Ammonia was driven off by NaOH and absorbed in HCl. NH_4Cl was recrystallized 2 times and determined in the same way as chlorine (Table 3).

Table 3.

	NH_4Cl(g.)	$AgNO_3$(g.)	Atomic weight of N
A(ord. NH_4Cl, recryst. 3 times)	9.0116	28.6216	14.002
B	9.0116	28.6205	14.004
C	9.0116	28.6189	14.007

Ammonium ion is rich in N^{15}. Assuming that the atomic weight of nitrogen of NH_4Cl-A is 14.009, the atomic weights of nitrogen of NH_4Cl-B and -C are 14.011 aad 14.014, respectively. Percentages of N^{15} are 0.31 in NH_4Cl-B and 0.61 in NH_4Cl-C. The separation coefficients are 2.7 from the result of B and 2.6 from the result of C. It is not so difficult to separate N^{14} and N^{15} completely by the chemical methods. From these results it can be concluded that effect B is the decisive factor in the isotopic exchange reactions.

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