PRELIMINARY NOTE

KRYPTON FIXATION USING KrF$_2$ (III).

ENTRAPMENT OF KRYPTON INTO ZEOLITE 13X

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SUMMARY

The KrF$_2$ – zeolite 13X reaction at –40 °C results in entrapment of Kr in the zeolite. On heating, a portion of the entrapped Kr is retained up to 500 °C. The Kr loading is more than 8 cc(STP)/g at a storage temperature of 100 °C. The present work has suggested a feasibility of the zeolite encapsulation of radioactive krypton by a chemical procedure.

Because of the chemical inertness of krypton, all of the techniques so far developed for [85]Kr fixation are based upon its physical properties or physical phenomena [1]. In the 1960's, many noble-gas compounds were prepared by other workers [2]. The discovery of the existence of a Kr compound, KrF$_2$, has urged us to utilize it for the chemical fixation of Kr. In view of the high chemical-reactivity of KrF$_2$ at low temperatures, we expected a plugging of zeolite pores to take place on absorption to confine the Kr. In the previous work [3], a screening test has been made for several zeolites and retention of Kr was noticed on zeolites 5A and 13X. The present work was carried out to probe both the mechanism of the KrF$_2$– zeolite 13X reaction and also the possibility of fixing [85]Kr on the zeolite through this reaction.

The experimental apparatus and procedure used were the same as in the previous work [3]: in each experimental run, a dried zeolite-13X sample

(100 mg) in granular form (30~60 mesh) was reacted with KrF_2 vapor at -40 °C in a Monel container. KrF_2 vapor pressure is 1.7 torr (226 Pa) at -40 °C [4]. After the reaction, the remaining gas was analyzed with a mass spectrometer (Hitachi RMU-6L). The sample was then passed on to either Kr loading or leakage measurements. In the former case, the sample was heated stepwise up to 700 °C in a quartz tube and the Kr released from it was determined for each interval of 100 °C rise in temperature. In the latter case, we heated the sample isothermally in the Monel container at 100, 200, or 300 °C for 24~48 h, and traced the released Kr quantity as a function of time.

Table 1 shows the results obtained using 55 and 110 mg of KrF_2. The 2nd to 4th columns represent the composition of the remaining gas; the 5th to 11th columns, the Kr quantities released for each 100 °C rise in temperature; and the 12th column, the Kr loading which is the sum of the released Kr amounts. The main components of the remaining gas were Kr and O_2; neither F_2, HF, nor SiF_4 were detectable. Lack of SiF_4 indicates that the reaction took place in the pores. The appearance of O_2 reveals this reaction to be a partial fluorination of the SiO_2 and AlO_2 groups of the zeolite*, e.g.,

$$KrF_2 + SiO_2 \longrightarrow Kr + 1/2\ O_2 + SiOF_2 \ .$$
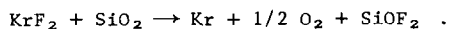
Therefore, the ratio of the Kr to O_2 concentration, in the table, should be equal to two if no Kr was trapped in the sample, and this holds approximately for the first case. Doubling the KrF_2 quantity (110 mg), however, decreased the Kr/O_2 ratio and brought about a remarkable increase in Kr loading. Evidently, the absorption of KrF_2 results in confinement of the Kr, although the absorptions of many other gases into zeolites are only due to their physical adsorptions.

We have interpreted this phenomenon as follows. In zeolite 13X, the pores through which KrF_2 molecules can pass are its α-cage with an entrance diameter of 8 Å. This entrance is circumscribed by a ring of 12-oxygen atoms [5]. On absorption, KrF_2 molecules replace the oxygen by fluorine atoms. The bonded F atoms distort inwardly the cage due to the repulsive force between them. Thus, a Kr atom is held in the cage by the repulsive energy between it and the fluorine atoms. The large entrance diameter needs the replacement of several oxygen atoms of the ring in

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*The composition of dried zeolite 13 X is expressed as $Na_{86}(AlO_2)_{86}(SiO_2)_{106}$

TABLE 1

Composition of the remaining gas, and the Kr quantity from the zeolite samples after their reactions with KrF_2.

Zeolite 13X samples (100 mg) were treated at $-40°C$ with 55 or 110 mg of KrF_2 for 1.5~3.0 h. The 2nd to 4th columns represent the composition of the remaining gas. The samples were than heated stepwise up to 700°C. The 5th to 11th columns show the Kr quantity released from the samples for each 100°C rise in temperature; and the 12th column, the Kr loading which is the sum of the released Kr quantities.

KrF₂ quantity introduced, mg	Composition of the remaining gas, %			Kr quantity released from the zeolite sample on heating, cc(STP)-Kr/g-zeolite							Kr loading, cc(STP)-Kr/ g-zeolite
	Kr	O₂	Others (CO₂, N₂, H₂O)	Temperature, °C							
				25 to 100	100 to 200	200 to 300	300 to 400	400 to 500	500 to 600	600 to 700	
55	60.0	32.3	7.7	0.2	0.2	0.0	0.1	0.2	0.0	0.0	0.7
110	43.3	41.4	15.6	0.2	1.1	0.8	1.7	3.7	2.2	0.0	9.7

order for reduction to block the exit of Kr atoms. This is reflected in
the difference in Kr loading between the 1st and 2nd cases in the table.

In the leakage measurement, the release of Kr became indiscernible
($\ll 10^{-3}$ cc(STP)/g.h) about 15 h after the temperature had reached a given
temperature, T_1. The container was then evacuated, cooled, and reheated;
further Kr release from the sample did not occur until the temperature
exceeded T_1. Thus, of the Kr trapped by the reaction, only 9.3, 25.9,
and 33.3 % evolved during heating at 100, 200 and 300 °C, respectively.
These results indicate that a dominant factor for the Kr release is an
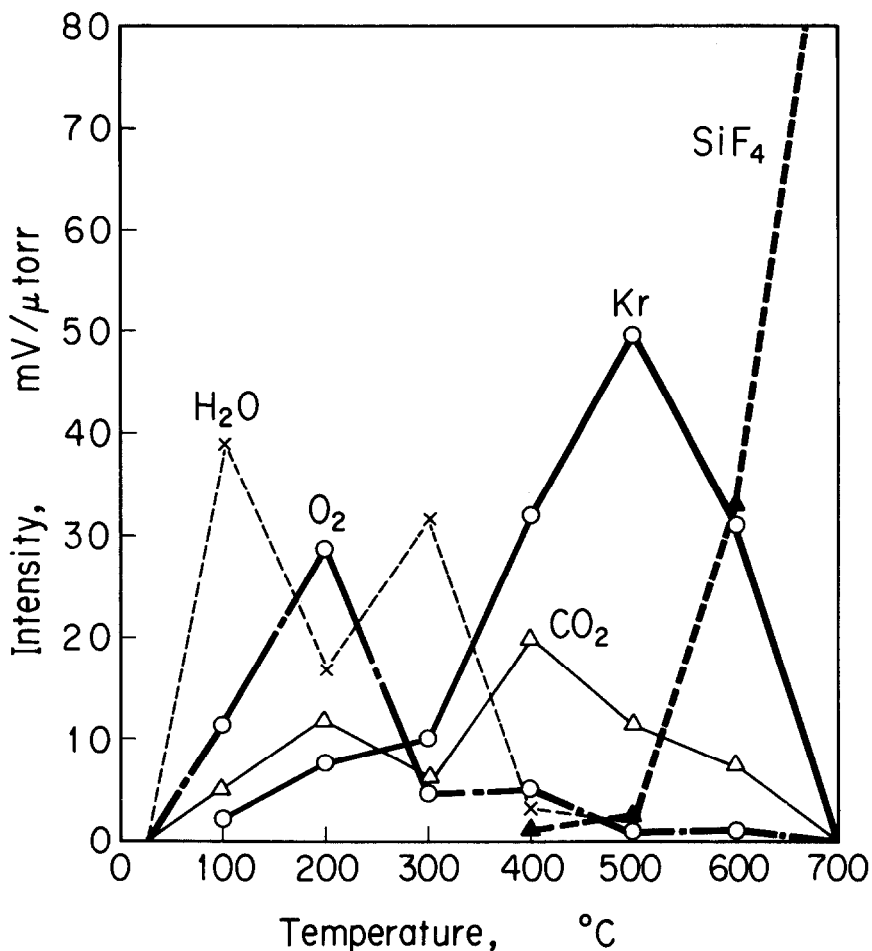activated diffusion process [6]. As the temperature increases, the

Fig. 1. Temperature dependence of mass-spectrographic intensities of the
gases which were released from the zeolite sample (100 mg) having been
treated with KrF_2 (110 mg) at -40 °C for 3 h.

vibrational energy of the Kr atoms in the cages increases. Of these, only a fraction which has obtained an energy larger than the repulsive energy diffuses out of the cages.

Besides Kr, the sample liberates O_2, H_2O, CO_2, and SiF_4 upon heating. Fig. 1 illustrates the plots of their mass-spectrographic intensities against temperature. Beyond 500 °C, SiF_4 alone was generated in a large quantity. This phenomenon is ascribable to the disproportionation of the partially-fluorinated SiO_2 group, e.g.,

$$2\ SiOF_2 \longrightarrow SiO_2 + SiF_4 \quad .$$
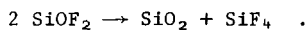
Since these reactions disintegrate the zeolite lattice, kr atoms cannot remain in the pores beyond 500 °C.

Storage temperature around 100 °C make it possible to fix the radioactive krypton from nuclear facilities using the present process. The table has suggested that the Kr storage should be more than 8 cc(STP)/g at 100 °C. Thus, the present work has revealed a feasibility of the zeolite encapsulation of Kr by a chemical procedure.

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