

Diffusion of Krypton in Cesium and Rubidium Iodide; A Comparison of Results Obtained Following Reactor Irradiation and Ion Bombardment

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The present study shows that under suitably chosen conditions, the same results of rare gas diffusion coefficients can be obtained in samples which are reactor irradiated to produce a homogeneous concentration of rare gas, and in samples that are labeled with rare gas by controlled ion bombardment. In the present study, the diffusion of krypton in RbI and CsI was found to follow the empirical rule of yielding activation enthalpies in the range $(1.4 \pm 0.2) \times 10^{-3} T_m$ eV, with T_m = melting point in °K. Trapping of rare gases (gas-gas or gas-damage interactions) was observed at high gas concentration.

Rare gas diffusion constants are usually determined by measuring the integral amount of gas that diffuses out of the specimen, i. e. the amount of gas that is released from the solid. In the early investigations, reactor irradiation was used to produce the rare gas atoms in the solid by a suitable nuclear reaction [fission, (n,γ) , (n,α) , (n,p) etc.]. Since these reactor irradiated specimens contained gas throughout the solid, there was frequently an overlapping of surface and bulk effects, e. g. a fast initial release, the so-called "burst", was observed. In samples containing pre-existing defects or at longer irradiation exposure leading to higher concentrations of radiation damage or higher gas concentrations, the release was retarded due to a "trapping" of gas atoms, i. e. to gas-damage or gas-gas interactions. Since these processes frequently occurred simultaneously in reactor irradiated samples, the diffusion constants deduced from the composite release curves had sometimes little or no physical significance.

To separate these processes, controlled ion-bombardment with well defined ion beams was chosen as a second alternative to label solids with rare gas because of its various advantages: with varying energy, the position of the gas (or median range of the gas ions) with respect to the surface can be chosen at will thus enabling a separation of surface and bulk effects; by varying the ion dose, the gas concentration can easily be varied without changing the purity of the specimen thus avoiding the many disturbing impurities that are produced during reactor irradiation; the specimen can easily be handled

and used without waiting times between labeling and release experiment whereas reactor irradiated samples are frequently highly radioactive and waiting times are necessary if all or part of the gas atoms are not produced directly but originate by radioactive decay of a mother substance; the effect of damage or *specific* impurities on release can easily be studied in double bombardments.

Careful investigations performed in this way and using the ion bombardment technique lead to a clear separation of the various processes that contribute to the overall release. These processes were grouped into a system of stages. On the other hand, some difficulties were observed in ion bombardment studies as well, the main one being the possibility of evaporation leading to the release of the rare gas. Since the ranges (penetration depths) of the rare gas atoms in ion bombardment work usually vary between a few Å up to about 1 μm , and in most experiments are of the order of 10^2 Å, evaporation losses of the order of one or a few $\mu\text{g}/\text{cm}^2$ surface cause an essential release but are difficult to measure. If the activation enthalpy, ΔH , for gas diffusion is less than the ΔH for vaporization, evaporation will dominate the release at high temperatures.

Therefore, it was early felt that a combination of the techniques of reactor irradiation (in the last years mainly employed by the schools of K. E. ZIMEN, Hahn-Meitner-Institut, Berlin (F. FELIX and coworkers) and of T. S. ELLEMAN, North Carolina State University) and of controlled ion bombardment (in the last years mainly employed by C. JECH, R. KELLY, E. V. KORNELSEN, G. SØRENSEN and the author) should be performed in order to obtain a

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maximum of reliable information. The first obvious system was that of fission xenon and UO_2 since many investigations had been made in this system because of its importance in reactor technology. The results¹ lead to a first understanding of the mechanism of undisturbed fission gas diffusion in uranium oxide, UO_2 , and the retarded release of gas (trapping) and the formation and annealing of radiation induced defects as observed in transmission electron microscopy could be correlated. Later, a similar combination of the two techniques was performed in a study of the diffusion of fission xenon in uranium monocarbide, UC^2 .

Another challenging system for a comparison of data obtained with reactor irradiated or ion bombarded crystals would be the alkali halides.

Unfortunately, for many years, *argon diffusion* was predominantly studied in reactor irradiated potassium halides since suitable isotopes of argon are easily formed by (n,p) reactions of the cation, whereas the heavy rare gases *krypton, xenon, and radon* were mostly used in the ion bombardment studies since the only argon isotope readily available for ion bombardment work, Ar-41 , has an inconveniently short half life of 1.82 h only. Preliminary ion bombardment studies showed that the mobility of argon in alkali halides can be greatly different from the mobility of the heavier rare gases³⁻⁵. Therefore, a comparison between the two techniques as applied to alkali halides seemed premature so far.

Recently, however, detailed results on the diffusion of heavy rare gases in reactor irradiated cesium iodide⁶⁻⁸ and rubidium iodide⁹ have been published thus greatly extending the earlier data of KALBITZER¹⁰. Therefore, it seemed to be of interest to perform an investigation on the release following ion bombardment and to compare the results.

Experimental

Single crystals of CsI and RbI were cut or cleaved from pieces purchased from Harshaw (Cleveland, Ohio) and pre-annealed in vacuo. Radioactive Kr-85 was introduced into the crystals using the heavy ion accelerator¹¹ of the Institute of Physics, University of Aarhus. A constant energy of 500 keV was used, and the integrated ion doses were varied between 2×10^{12} and 4×10^{15} Kr-ions/ cm^2 . Release measurements were performed isochronally in vacuo (about 10^{-5} Torr) with 5 min holding times at each temperature. The heatings were spaced at intervals of $\geq 50^\circ\text{C}$ to keep the effect of preceeding annealings small.

Theoretical

The mathematics needed to evaluate diffusion coefficients and to calculate activation enthalpies, ΔH , have been published previously^{3, 12}. The median range, R_m , of the krypton ions was assumed to be 7600 Å in CsI and 8000 Å in RbI , based on range measurements with other alkali halides¹³. An error in the range would yield a parallel shift of the Arrhenius line and hence affect the pre-exponential term, D_0 , only. Besides the evaluation in the Arrhenius diagram, activation enthalpies were deduced directly from the release curves (curves of fractional release, F , versus temperature, T) assuming an idealized range of the pre-exponential rate constant, $k_0 = 10^{15 \pm 1} \text{ sec}^{-1}$, as is usual in this type of work (e. g. ^{3, 4, 12})^{12a}.

Results and Discussion

Fig. 1 shows the results obtained for ion bombarded RbI together with literature data for reactor irradiated RbI . The present ion bombardment data can be grouped around two parallel lines c and d representing the lower and the higher bombardment doses (gas concentrations) (provided it is correct to draw a single line for the high dose data since at

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¹³ J. L. WHITTON and HJ. MATZKE, Can. J. Phys. **44**, 2905 [1966].

^{12a} This range of k_0 corresponds to a range of D_0 of $3 \times 10^{-1 \pm 1} \text{ cm}^2 \text{ sec}^{-1}$ as is typical for most data on solute diffusion. The assumption of this range enabled a first separation of the various processes contributing to the overall release in complex systems. As shown in Ref. ¹⁹, the effective D_0 can be different by a factor of $\gamma_i/\gamma_T C_T$ where the γ 's are the appropriate entropy factors $\exp(S/k)$ for the interstitial sites (i) and traps (T), the molar fraction of which is C_T .

both high and low temperatures the data points tend to fall *above* this line). The corresponding ΔH is 1.45 ± 0.05 eV for both lines, the pre-exponential constants, D_0 , are 5×10^4 and 3×10^3 cm²/sec for line c and d, respectively. The ΔH 's deduced from the gas release curves (F vs. T curves) are somewhat lower due to the assumed idealized range of $D_0 = 3 \times 10^{1 \pm 1}$ cm² sec⁻¹, and are 1.05 ± 0.1 eV for the lower dose and 1.15 ± 0.1 eV for the higher

dose. At the lowest temperature of 135 °C and for all doses used, the diffusion coefficients are higher than expected and do not fit to lines c and d. The scatter of the data is comparable to that of data obtained following reactor irradiation, as indicated by the black dots around line b.

Fig. 2 shows the results obtained for krypton diffusion in ion bombarded Cs I together with literature data on xenon diffusion in reactor irradiated or

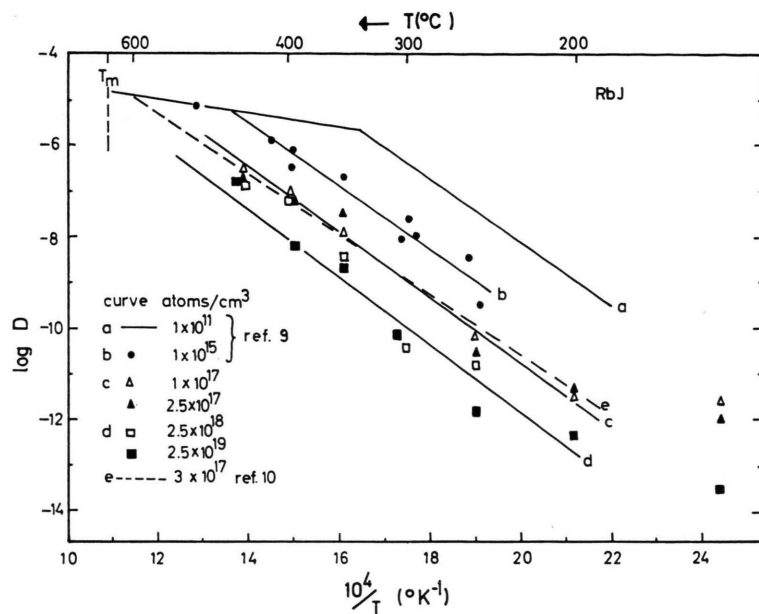


Fig. 1. Arrhenius diagram of the diffusion of krypton in Rb I. Included are literature results of FELIX⁹ and KALBITZER¹⁰. A gas concentration of 10^{17} atoms/cm³ corresponds to a bombardment dose of about 1.6×10^{13} ions/cm².

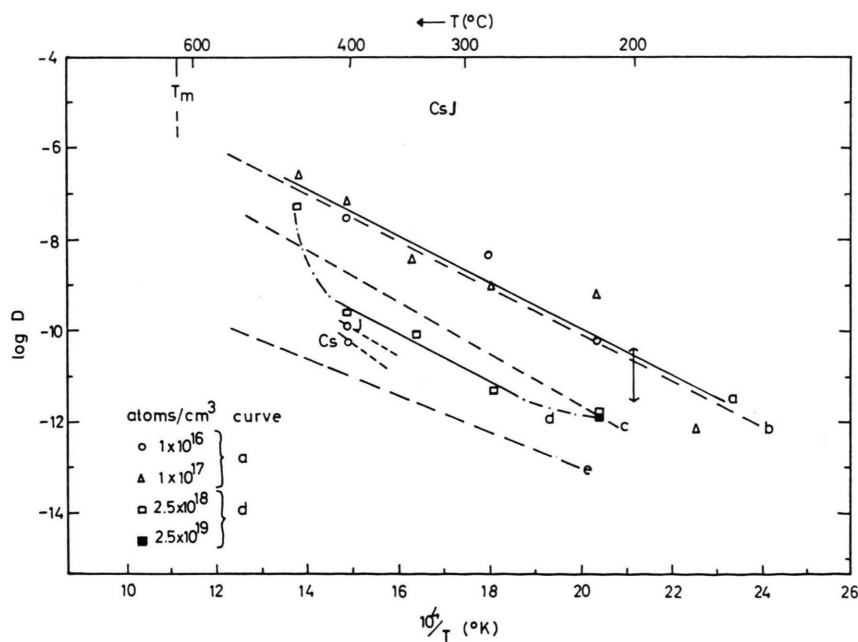


Fig. 2. Arrhenius diagram of the diffusion of krypton in Cs I. Included are literature results of ELLEMAN, FOX, and MEARS⁶, of FELIX and MEIER⁷ and of KALBITZER¹⁰ on the diffusion of xenon in Cs I. The arrow indicates the scatter in the literature results. The self-diffusion measurements of LYNCH¹⁴ are indicated around 400 °C by the two small dashed lines.

curve	atoms/cm ³	Ref.
b	9×10^{12}	6
c	2×10^{16}	7
e	1×10^{18}	10

"iodine labeled" (see below) Cs I as well as on self-diffusion in Cs I. No data are available for the system Kr/Cs I, but the differences in diffusion rates^{13a} between Xe and Kr should be negligible since even Ar diffuses in Cs I at rates (identical ΔH , $D_0^{\text{Ar}} = 1.5 D_0^{\text{Xe}}$) very similar to those of xenon⁸. Again, the data for the two lower doses can be grouped together (line a, $\Delta H = 1.0 \pm 0.05$ eV, $D_0 = 0.65$ cm² sec⁻¹). The diffusion coefficients for the two higher doses are smaller, especially between about 250 to 400 °C, where they can be grouped around line d (ΔH again 1.0 eV, $D_0 \approx 0.02$ cm² sec⁻¹). At 220 °C and especially at 450 °C, however, the diffusion coefficients are much higher than would correspond to line d. The ΔH 's deduced from the gas release curves (F vs. T curves) assuming the idealized range of $D_0 = 3 \times 10^{-1 \pm 1}$ cm² sec⁻¹ would be 1.02 ± 0.1 eV for the lower doses (hence good agreement with the value deduced from Fig. 2) and 1.13 ± 0.1 eV for the higher doses. The scatter of the data is again comparable to that of data obtained following reactor irradiation or "damage-free labeling" by introducing into Cs I I-133 that decays into Xe-133 (see arrow in Fig. 2).

The present results on ion bombarded samples agree well with the literature data on specimen where reactor irradiation and nuclear reactions were used to produce the rare gases in the crystals. The diffusion constants, ΔH and D_0 , published so far, are

summarized in Table 1 together with the present results. In addition, evaluation of the present data from an Arrhenius-type diagram and direct computation of ΔH 's from the F vs. T curves yields comparable results, the agreement being particularly satisfying for Cs I. The ΔH 's for the lower doses can be expressed in relation to the melting point, T_m in °K, as $\Delta H = 1.13 \times 10^{-3} T_m$ eV for Cs I and $\Delta H = 1.58 \times 10^{-3} T_m$ eV for Rb I which is in approximate agreement with an empirical rule¹⁵ stating that the ΔH for gas diffusion at low gas concentration should fall into the range

$$\Delta H = (1.4 \pm 0.2) \times 10^{-3} T_m \text{ eV}.$$

For such a diffusion, the undisturbed mobility of single gas atoms was assumed¹⁵. One of the authors suggested previously on basis of doping and channeling experiments^{3, 16, 17} that the mechanism for such a diffusion, in the alkali halides KCl, KBr, and NaCl, involves the mobility of single gas atoms in small vacancy clusters, most probably divacancies (neutral vacancy pairs). A similar mechanism was later suggested by ELLEMAN et al.⁶ for Cs I, and by PRONKO and KELLY for RbCl¹⁸, based on a comparison of their data with theoretical calculations of NORGETT and LIDIARD¹⁹. The latter authors calculated, for Kr-diffusion in Rb I, the following ranges (depending on the potential and gas-ion interaction constants used) of energies:

Substance	gas	gas concentration (atoms/cm ³)	D_0 (cm ² sec ⁻¹)	ΔH (eV)	ref.	technique of
Rb I	Kr	1 to 2.5×10^{17}	5×10^4	1.45	p. s.	ion bomb.
		2.5 to 25×10^{18}	3×10^3	1.45	p. s.	ion bomb.
		1×10^{11}	1.3×10^6	1.41	9	react. irr.
		1×10^{15}	8×10^4	1.41	9	react. irr.
		3×10^{17}	8×10^2	1.35	10	react. irr.
Cs I	Kr	1 to 10×10^{16}	0.65	1.0	p. s.	ion bomb.
		2.5 to 25×10^{18}	(0.02)*	(1.0)*	p. s.	ion bomb.
	Xe	9×10^{12}	0.57	1.01	6	I-doping
		4 to 150×10^{14}	≈ 0.05	≈ 1.0	6	react. irr.
		2×10^{15}	2	1.14	7	react. irr.
		2×10^{16}	0.65	1.14	7	react. irr.
		8×10^{13}	0.3	0.98	8	react. irr.
		1×10^{18}	1×10^{-5}	0.8	10	react. irr.

Table 1. Diffusion constants for rare gas diffusion in Rb I and Cs I. (p. s. = present study.)

* Tentative values since the straight line d in Fig. 2 is not well defined.

^{13a} In contrast to Rb I, practically identical diffusion rates are observed for various rare gases in Cs I. Ref. ⁸ shows that the diffusion coefficients for Ar and Xe differ only slightly, and the present study proves that also the diffusion coefficients for Kr are very similar to those for Ar and Xe.

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¹⁸ P. P. PRONKO and R. KELLY, to be published.

¹⁹ M. J. NORGETT and A. B. LIDIARD, Phil. Mag. **18**, 1193 [1968].

binding in anion vacancy	1.00 to 1.81 eV;
binding in cation vacancy	0.96 to 1.23 eV;
binding in vacancy pair	1.13 to 1.76 eV;
solution in interstitial site	0.95 to 1.80 eV;
interstitial diffusion	0.22 to 0.30 eV;
experimental result	1.45 ± 0.05 eV.

Evidently, the experimental results would be compatible with the gas interacting with single vacancies or with vacancy pairs. In analogy to the above mentioned alkali halides, we would favour the mechanism involving divacancies as the most probable one. Similar conclusions can be drawn for heavy rare gas diffusion in CsI. Here, in addition, the diffusion coefficients for self-diffusion have been measured¹⁴ and are much lower than those of rare gases, thus again favouring an independent mechanism for gas mobility.

It should be noted that the present study did not yield any indication of a high temperature release process in RbI having a low ΔH of about 0.3 eV (see upper part of curve a in Fig. 1 and ref. 9) which would be compatible with the above calculated value for interstitial diffusion. In CsI, such a process was not observed either in the previous literature studies.

The present data extend the range of gas concentrations used previously to still higher values. With increasing gas concentration (bombardment dose), lower diffusion coefficients are observed with a saturation being indicated at concentrations of about 2.5×10^{18} atoms/cm³ since a further increase in gas concentration to 2.5×10^{19} atoms/cm³ does not lead to a substantial further decrease in D -values. Such a decrease indicates the well known trapping of rare gas atoms (gas-gas or gas-damage interactions). Parallel lines in the Arrhenius diagrams are indicated for the different concentrations implying similar (or identical) ΔH 's. Most other substances (e. g. ²) show an increased ΔH whenever trapping occurs. Even in the present study, the data points tended to fall together at high temperatures, independent of dose. At low temperatures, too high D -values were found indicating a faster mechanism of release. Similar observations were recently reported for Kr-diffusion in KCl and RbCl¹⁸.

For CsI, the present results for fairly high gas concentrations of 1×10^{16} and 1×10^{17} atoms/cm³ agree with the literature data for lower concentrations (9×10^{12} and 1×10^{14} atoms/cm³) whereas the literature data for concentrations between 2×10^{15} and 2×10^{16} atoms/cm³ fall between the present cur-

ves a and d thus indicating trapping. In principle such a result would be expected because of the different experimental conditions of having a thin layer containing the gas in the ion bombardment work on the one hand and a homogeneously labeled big crystal in reactor irradiation studies on the other hand. As shown previously^{12, 15}, the fraction, G , of gas atoms that will escape without getting trapped at radiation damage or in defect clusters is simply

$$G = \exp(-p/L)$$

where p = depth of the gas atom beneath the surface and L = diffusion length for trapping. Hence, the fraction G is expected to be higher in ion bombardment work because of the smaller mean p . However, no such effect was observed with RbI. Though the reason for this discrepancy is unclear one should bear in mind the different crystal structures of the two substances (RbI = NaCl-type; CsI = CsCl-type).

The agreement of the present low dose data for CsI with those of ELLEMAN, FOX, and MEARS⁶ who used "iodine doped" CsI is particularly striking. Elleman et al. employed an ingenious technique to obtain Xe-labeled CsI with a minimum of damage. They grew CsI single crystals containing I-133 which, by β -emission, decays into Xe-133. These Xe-atoms receive a maximum recoil energy of 12 eV which should be insufficient to produce more than about one vacancy. The agreement of the data obtained with these crystals with those of the present study (or with Elleman's low dose fission recoil doped specimens⁶) indicates one of two possibilities: either trapping of rare gases in CsI does not become important before unusually high gas concentrations are reached, or essential damage is created in CsI even by I-doping, e. g. by mechanisms similar to those of colour center production or sputtering in alkali halides (measurable ejection of atoms from e. g. NaCl or KI can be obtained with 10 eV electrons or 5 eV photons and holes can easily be obtained in alkali halides during electron bombardment at slightly higher energies²⁰).

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²⁰ P. D. TOWNSEND and D. J. ELLIOTT, presented at the Int. Conf. on Atomic Collision Phenomena in Solids, Sussex, U. K. 1969.