Rare Gas Diffusion in NaCl

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The mobility (diffusion and trapping) of the heavy rare gases Kr, Xe, and Rn in pure and doped NaCl single crystals was measured following ion bombardment to various integrated doses (10^8 to 2×10^{16} ions/cm^2) and at energies between 30 and 500 keV. No obvious effect of doping on release was found. At low gas concentrations, release was compatible with volume diffusion yielding an activation enthalpy, ΔH, of 1.5 ± 0.2 eV. This value was obtained for both very low and very high bombardment energies (≈ 1 and 500 keV) thus indicating that the same release mechanism is operative near the surface and in the bulk material. For this release mechanism, a mobility in small vacancy clusters was suggested. At higher gas concentrations, the release was shifted towards higher temperatures. This retarded release was explained by transient trapping, i. e. by gas-gas or gas-damage interactions, and was shown to have a partially single jump character. Again, the result was the same for low and high bombardment energies.

The mobility of rare gases, which was first studied in nuclear fuels because of reactor safety and fuel swelling problems, has since been realized to be affected by a variety of factors like gas-concentration, pre-existing defects, various types of radiation damage and their annealing, phase transformations, proximity of the gas to a surface etc. Therefore, much work has been carried out both on nuclear materials and on substances that are physically well understood, to resolve and understand the different processes contributing to the overall release. The present study contributes to the general knowledge of the behaviour of rare gases in solids by providing new data on NaCl and, in addition, by studying the kinetics of the final release at higher gas concentrations, i. e. under conditions when gas-gas or gas-damage interactions would be expected. This was possible since, for the first time, high energies (up to 500 keV) were employed in the bombardment of ionic crystals.

1. Experimental

Single crystals of NaCl (Harshaw, Cleveland, Ohio), both nominally pure and containing an added amount of 500 ppm $CaCl_2$, were cleaved and bombarded with Kr- and Xe-ions of energies between 30 and 500 keV. The Chalk River * isotope separator [1], the Aarhus isotope separator [2], and the heavy ion accelerator [3] of the Institute of Physics, University of Aarhus were used as ion guns to obtain integrated ion doses between 8×10^{10} and 2×10^{16} ions/cm^2. 85 keV Rn at a dose of about 10^8 ions/cm^2 was introduced using nuclear recoil [4].

Following the bombardments, diffusion measurements were carried out by alternately heating the samples isothermally in air with hold times of 5 or 15 min and then cooling to room temperature for counting. The heatings were spaced at intervals of $\geqq 40$ °C to keep the effect of preceeding annealings small.

Some additional data on low energy Kr-bombardments, obtained by means of a Tesla, i. e. high-frequency, discharge apparatus [5] were courteously supplied by Dr. C. JECH, Institute of Materials Research, McMaster University, Hamilton, Ontario, Canada.

2. Theoretical

The mathematics needed to analyse the present data on gas release from ion bombarded samples have been published previously [6–9]. To calculate the activation enthalpy, ΔH, the median range, R_m, of the gas has to be known. A previous study on

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* These experiments were carried out during the stay of one of the authors (HJ. MATZKE) at the Chalk River Laboratories during 1964—1966.

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NaCl[10] has shown that within the dose range used, R_m is practically independent of dose and is about 920 Å for 40 keV Xe-ions. Due to their lower atomic number, 30 keV Kr-ions should have about the same range. For the higher energy Kr-ions, a linear relation between R_m and energy was assumed, whereas a value of 1400 Å was chosen for 85 keV Rn. To evaluate the data on Tesla-labeled NaCl, a value of 6 atoms layers was used for R_m [9]. Furthermore, a range of values was assumed for the pre-exponential rate constant k_0 ($10^{15\pm1}$ sec^{-1}) in calculating both ΔH's and theoretical peak widths. This range for k_0 was chosen as it agrees best with most of the reliable diffusion data, at least at tracer concentrations.

Fig. 1 shows some theoretical release curves for a volume diffusion process with $\Delta H = 1.95$ eV (45 kcal/mole) and $k_0 = 10^{15}$ sec^{-1} ($D_0 \approx 0.3$ cm^2/sec). Increasing the bombardment energy (1, 5, 10, 20, 40, 100, 300 keV) shifts the release curves towards higher temperatures. (For these calculations, a linear relation between R_m and energy was assumed.) Simultaneously, the release curves cover a broader temperature interval. The two dotted curves a) and b) show the effect of a change in k_0: both curves are for 40 keV, but for $k_0 = 10^{14}$ sec^{-1} and $k_0 = 10^{16}$ sec^{-1} corresponding to D_0's of about 0.03 cm^2/sec and 3 cm^2/sec.

Varying the annealing time is expected to yield a similar shift in temperature, e. g. at an energy of 40 keV, the release curve should be shifted by about 35° towards lower temperature, if the annealing time is increased from 5 to 15 min. These two annealing times were used in the present study.

3. Results

The experimental results are shown in Figs. 2 – 5 and summarized in Table 1. Fig. 2 shows the release of Xe (40 and 43 keV) and Rn (85 keV) from pure and doped NaCl at low bombardment doses (10^8 to about 10^{11} ions/cm^2). No obvious effect of doping is observed though the data points for the release of *xenon* from the doped crystals tend to be below those for the nominally pure samples. Both release curves are compatible with volume diffusion yielding $\Delta H = 1.5 \pm 0.2$ eV for the diffusion of Rn and $\Delta H = 1.6 \pm 0.2$ eV for the diffusion of Xe. For identical diffusion rates of Rn- and Xe-atoms, one would expect practically identical release curves as the effect of the higher energy of the Rn-atoms (85 vs 40 to 43 keV) is roughly compensated by the choice of the bombardment geometry (random angle of incidence for Rn, vertical incidence for Xe). However, the release of Rn is seen to occur at lower temperature than the release of Xe although the temperature intervals for release (about 200 to 500 °C) are nearly identical. These temperature intervals and the one between $F = 0.1$ and $F = 0.9$ ("peak width", see Table 1) are somewhat bigger than would be expected for a pure volume diffusion process.

Gas	energy keV	dose ions/cm^2	peak width* exp.	peak width* calc.	ΔH eV
Kr	30	3×10^{12}	200	185	1.5
	60	3×10^{12}	137	200	1.5
	150	3×10^{12}	—	215	1.4
	450	3×10^{12}	116	265	1.4
	300	1×10^{13}	150	305	1.7
	500	1×10^{13}	235 (175)	315	1.6
	30	6×10^{13}	180 (100)	200	1.6
	60	6×10^{13}	110 (70)	220	1.6
	150	6×10^{13}	110 (80)	250	1.6
	450	6×10^{13}	90 (75)	290	1.5
	500	1×10^{15}	165 (135)	355	1.8
	300	1×10^{16}	130	340	1.9
	500	1×10^{16}	110	355	1.8
	Tesla	(0.9 sec)	135	100	1.5
	Tesla	(3.0 sec)	90	150	2.4
Xe	40	8×10^{10}	260	200	1.6
	40	4×10^{13}	265 (135)	255	2.0
	40	2×10^{16}	185 (130)	260	2.1
	Tesla	(0.1 sec)	155	100	1.6
	Tesla	(3.0 sec)**	85	150	2.4
Rn	85	10^8	210	195	1.5

* The definition of peak width for the Tesla data is taken as $T_{1/2}$, the width at half height, while that for the remaining higher energy data is taken as $T_{90\%} - T_{10\%}$. For composite curves, the widths corrected for the presence of a second process are given in brackets. The calculated values of peak widths have been obtained by applying the formulae of ref. [9].

** Prebombarded for 3.0 sec with inactive Kr, then labeled for 0.1 sec with radioactive Xe.

Table 1. Observed activation enthalpies (ΔH's). An initial distribution of the gas of the type "e^{-x}" has been assumed for all calculations. The uncertainties in the ΔH's due to the assumed range of k_0's i. e. $10^{15\pm1}$ sec^{-1}, are ± 0.2 eV. The activation enthalpies for high bombardment doses are apparent values only, since kinetics different from those of *pure* volume diffusion are indicated and since k_0 may be $\neq 10^{15}$ sec^{-1}.

Fig. 3 shows the corresponding release of Xe following 40 keV bombardments at intermediate or high doses (4×10^{13} to 2×10^{16} ions/cm^2). Again, no obvious effect of doping on release is observed,

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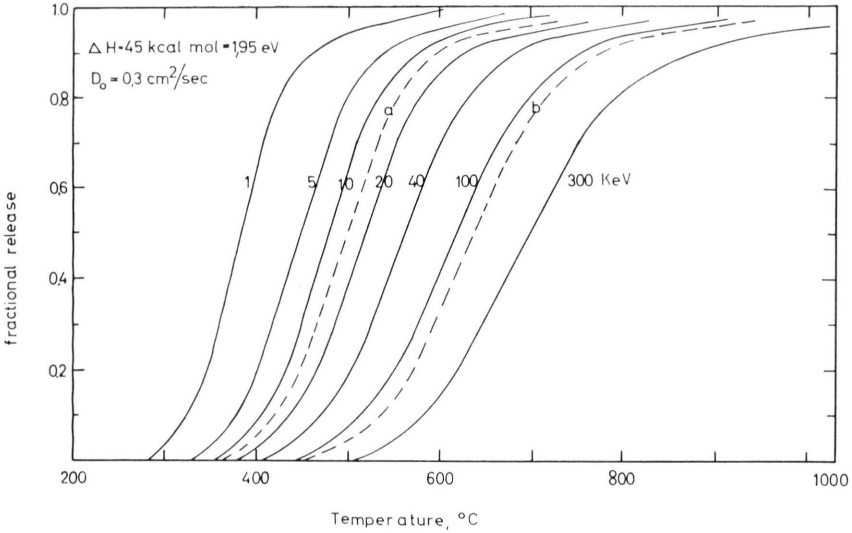

Fig. 1. Theoretically expected release curves for a volume diffusion process with $\Delta H = 1.95$ eV $= 45$ kcal/mole. The full curves are for $D_0 = 0.3$ cm²/sec and bombardment energies of 1, 5, 10, 20, 40, 100, and 300 keV, assuming a linear relation between energy and median range of the ions. The dotted curves a) and b) are for 40 keV and $D_0 = 0.03$ and 3 cm²/sec.

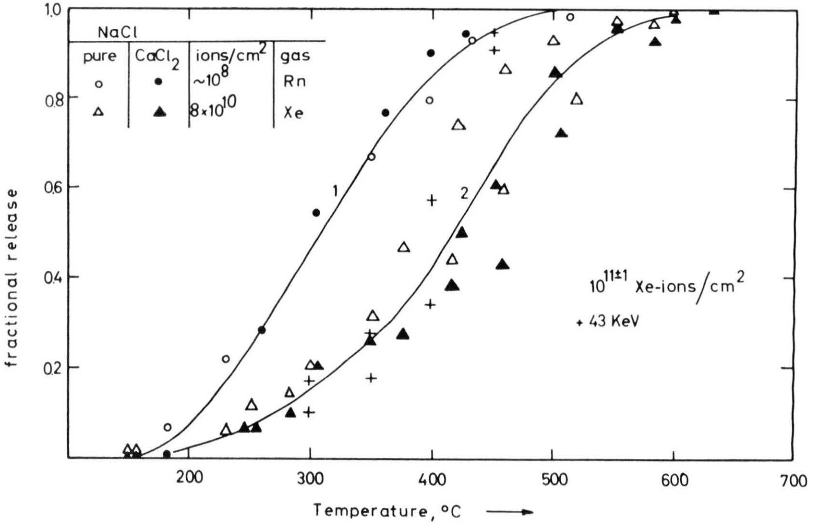

Fig. 2. Release of radon and xenon from pure and doped NaCl single crystals following low dose bombardment to energies of 40, 43, or 85 keV. The annealing time was 5 min, except for the 43 keV data where it was 15 min.

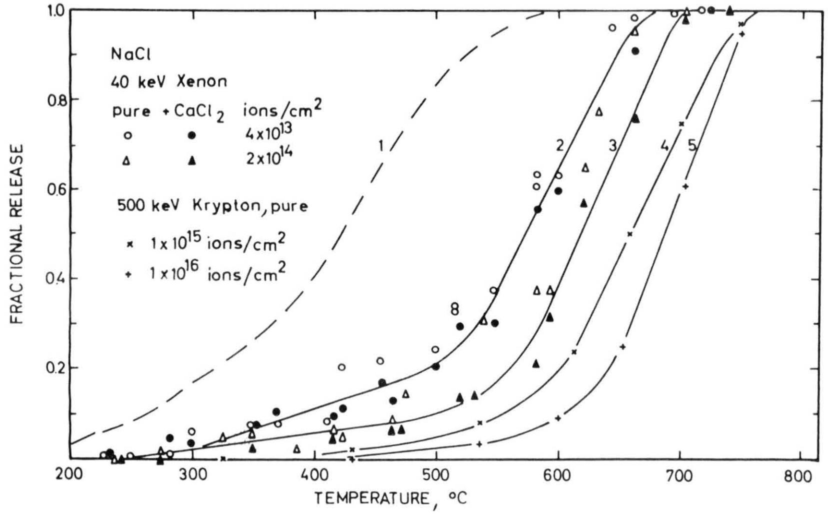

Fig. 3. Release of xenon from pure and doped NaCl single crystals following intermediate and high dose bombardement (2×10^{14} ions/cm² as erroneously stated in the fig.) at 40 keV. The annealing time was always 5 min.

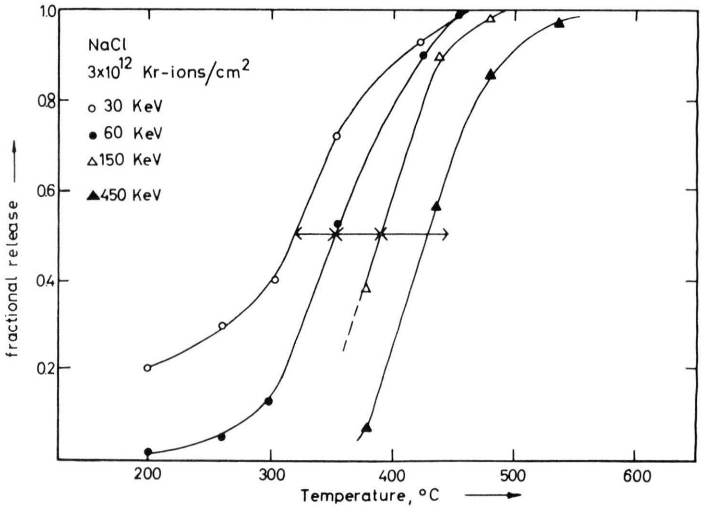

Fig. 4. Release of krypton from pure NaCl single crystals at a dose of 3×10^{12} ions/cm² and at bombardment energies of 30, 60, 150, and 450 keV. The annealing time was always 15 min.

though, as for xenon in Fig. 2, the release from the doped crystals tended to be slightly slower. However, the release curves are shifted towards very much higher temperatures as compared to the release curve following low dose bombardment (curve 1). Curves 4 and 5 show additional data for the release of krypton implanted at a high energy of 500 keV. All curves 2 to 5 consist of two parts: the first part covers the temperature interval from roughly 250 to 550 °C, i. e. that of curve 1, and comprises 4 to 20% of the overall release; the second part is steep, covers the temperature region from about 550 to 700 °C and comprises most (80 to 90%) of the release. The widths of the second parts are smaller than one would expect for a volume diffusion process (Table 1).

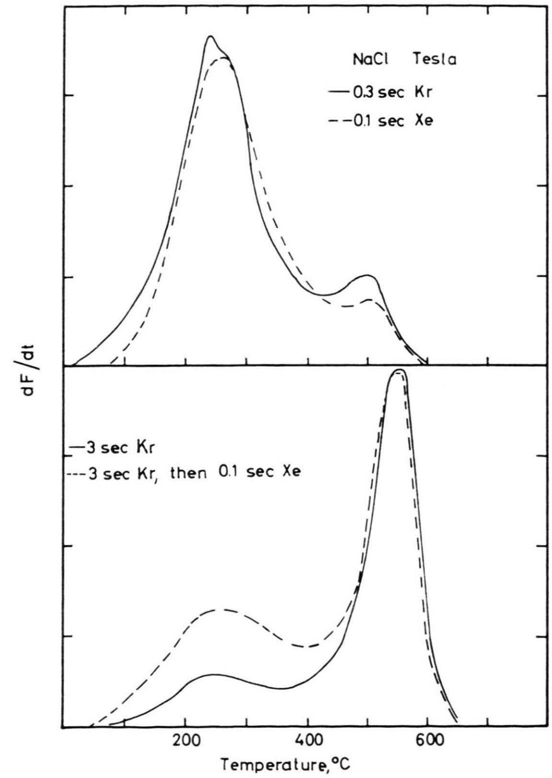

Fig. 5. Release of krypton or xenon from Tesla-labeled NaCl single crystals. The heating rate was 25°/min. The release rate dF/dt is in arbitrary units.

Fig. 4 shows the effect of bombardment energy (30, 60, 150, 450 keV) at a dose of 3×10^{12} ions per cm^2 on the release of Kr from pure NaCl. A corresponding series of experiments was performed at at dose of 6×10^{13} ions/cm^2. At the lower dose of 3×10^{12} ions/cm^2 (Fig. 4), the effect of increasing energy is (with the possible exception of the highest energy, 450 keV) that expected from theory: the arrows in Fig. 4 indicate the expected shift in temperature for a release of $F = 0.5$. At the higher dose of 6×10^{13} and in some runs at a dose of 1×10^{15} ions/cm^2, however, the release curves were slightly closer together than would be expected for a pure volume diffusion process. In addition, Table 1 shows that the "peak widths" were much smaller than expected.

In Fig. 5, some additional data on the release of Kr and Xe from Tesla labeled NaCl are presented. These data were supplied by JECH in extension of his earlier work on NaCl [5]. The doses obtained in Tesla labellings are not exactly known and depend on pressure and sticking factor but, for an estimate, they have been shown [11] to be roughly 10^{13} ions/cm^2 for 0.3 sec discharges and roughly 10^{14} ions/cm^2 for 3.0 sec discharges. At both doses, two peaks are observed. The peak centered at about 240 °C implies a ΔH of 1.5 ± 0.2 eV and is prominent at the lower dose, whereas the second peak at about 550 °C ($\Delta H = 2.4 \pm 0.2$ eV) dominates at the higher dose.

4. Discussions

4.1. Release at low bombardment doses

At low gas concentrations, i. e. bombardment doses between about 10^8 and 10^{11} ions/cm^2, the release of Xe and Rn (Fig. 2) is roughly compatible with a volume diffusion process with D_0 in the range $3 \times 10^{-1 \pm 1}$ cm^2/sec and $\Delta H = 1.5 \pm 0.2$ eV. The shapes of the release curves are similar to theoretical expectations, with "peak widths" that are comparable to, although slightly greater, than predicted. The release process also follows the empirical rules reported elsewhere [12] for volume diffusion of heavy rare gases: i) release is expected to start (median diffusion length about 10 atom layers/min) between 0.4 and 0.5 of the melting point on the absolute temperature scale. The "onset" temperatures of the present results, 210 to 260 °C (Fig. 2) correspond to 0.45 to 0.5 T_m. ii) the ΔH is expected to follow the relation

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

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hence ΔH is expected to be 1.5 ± 0.2 eV which agrees exactly with the measured value. iii) the ΔH for the gas should be about $80 \pm 10\%$ of the ΔH for the self-diffusion of the less mobile lattice ion. The ΔH for Na-ions is 1.8 eV while that for Cl-ions (and a vacancy mechanism) is 1.9 eV (e. g. [13, 14]); therefore, the ΔH for the gas is 79% of the ΔH for the slower Cl-ions, again in agreement with expectation. Hence we conclude that the gas is released via a normal volume diffusion process (also frequently referred to as "Stage II A (e. g. [15]).

It seems worth stressing that this process and the same ΔH are observed for differences in diffusion distances (ranges) of a factor of 2×10^3. This shows, that gas as near as 6 atom layers to the surface of a NaCl-single crystal behaves just in the same way as gas located deep in the solid. A similar conclusion has been reached by KORNELSEN [16] for ultraclean tungsten where surface effects were observed in the first 3 atom layers only.

A possible explanation for the fact (Fig. 2) that the release of Rn occurs at lower temperatures than the release of Xe might be that at the bombardment doses used for Xe (8×10^{10} to 10^{11} ions/cm^2), some trapping (see Section 4.2) was already occurring. In contrast to this result, the two gases showed the same release temperatures in KCl [9] and KBr [8]. This might indicate either that NaCl is more susceptable to radiation damage or else that trapping in NaCl occurs at lower doses than those required for trapping in KCl and KBr.

The data of Fig. 4 on Kr-release following bombardment to about 3×10^{12} ions/cm^2 yield the ΔH for volume diffusion but the "peak widths" are smaller than expected for a volume diffusion process. This may be due to an overlapping of trapping (Section 4.2) and volume diffusion that would be expected at such a dose.

The first peak of Fig. 5 can be attributed to volume diffusion as it i) yields the right ΔH, ii) shows about the right "peak-width" (see Table 1), and iii) is only prominent at the lower bombardment dose (0.1 or 0.3 sec discharge). A similar peak has already been described by JECH [5].

As to the diffusion mechanism, a mobility in small vacancy clusters, e. g. divacancies, is suggested as gas release is not obviously affected by doping. In contrast to the concentration of single Na- and Cl-vacancies, the concentration of divacancies is essentially not affected by doping. Divacancies are known to exist in NaCl and to contribute considerably to Cl-diffusion [13]. In addition, "channeling" experiments on the related substance, KCl, labeled with Rn, have yielded the direct experimental indication [17] that, at least at room temperature and at 200 °C, Rn does not occupy single K- or Cl-vacancies or diffuse via these sites. This leaves the alternatives of an interstitial mechanism or a mobility in small vacancy clusters. The latter mechanism seems to be preferable in view of the large size of the rare gas atoms (radius ≈ 2 Å) compared to the small (not spherical) interstitial holes of the NaCl-structure (half diameters between 0.9 to 1.4 Å, hence the radius of the biggest sphere fitting into these holes would be 0.9 Å).

The only other data on rare gas mobility in NaCl that are available in the literature [18-20] are for the light rare gases He ($\Delta H = 0.8 - 1.2$ eV) and Ar ($D_0 \approx 100$ cm^2/sec, $\Delta H = 1.4$ eV). Although the ΔH for Ar is comparable to those of the present work, the diffusion of Ar is considerably faster than that of Kr, Xe, and Rn due to the higher D_0. This is not surprising, however, as the diffusion of light rare gases is generally not directly comparable to that of heavy ones. In contrast to the latter, which show a similar release behaviour [12], the light rare gases can have both a different release mechanism at low doses [8, 9, 12, 21] and a much less pronounced trapping behaviour [21] (see also Section 4.2).

4.2. *Release at high bombardment doses*

At high bombardment doses ($\geqq 10^{13}$ ions/cm^2), higher temperatures were needed, to reach a given F-value as compared to the lower doses. The curves of Fig. 3 are shifted by 150 °C (4×10^{13} Xe-ions/cm^2) or 200 °C (2×10^{16} Xe-ions/cm^2) towards higher temperatures as compared to curve 1 (8×10^{10} Xe-ions/cm^2); the curves for a dose of 6×10^{13} Kr-

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ions/cm^2 were shifted by about 75 to 100 °C as compared to those of Fig. 4 (3×10^{12} ions/cm^2), and the dominant peak at the higher dose (3.0 sec discharge) in Fig. 5 lies 310 °C above that at the lower doses (0.1 to 0.3 discharge). Such a transient trapping effect[22] is known for many substances (e. g. [12]) including alkali halides (e. g. [9]) and is explained by an interaction between gas atoms and bombardment induced defects or other gas atoms[6, 23]. Due to this shift in temperature, the *apparent* activation enthalpies are higher than those at low doses by between 0.1 and 1.0 eV (see Table 1). However, it is not sure whether volume diffusion kinetics can be applied to these retarded releases. In the present work, high bombardment energies ($\gg$ 100 keV) were applied in the ion bombardment of ionic crystals for the first time. (Such energies have previously been used only with two metals, copper and silver, reported in two recent publications[24, 25].) These high energy runs (e. g. Fig. 4) show two novel features of the final retarded release: i) The "peak widths" are much smaller than would be expected for volume diffusion; the same is true, but less pronounced, for the high dose runs at lower energies (Figs. 3 and 5, Table 1. – The small peak width of the high dose peak at about 550 °C in Fig. 5 might by partly due to the onset of evaporation, as indicated by its slight asymmetry). ii) The spacing between release curves following high dose bombardments is sometimes smaller than would be expected from volume diffusion. Such behaviour was taken in a previous study[26] of potassium halides to imply a partially "single jump" character of the release of trapped gas; a true single jump process would have an even smaller "peak width" of only 40 – 50 °C and would not have any dependence on energy (range). These conclusions are compatible with the follwing picture: the gas atoms get immobilized (trapped) at bombardment induced defects (e. g. bigger vacancy clusters, dislocation loops, or bubbles), and the final release is either due to detrapping and a fast diffusion from defect to defect, or else to the onset of the mobility of these defects that then does not follow ideal volume diffusion kinetics.

An alternative model might also be envisaged similar to that discussed in ref. [27] in connection with gas-release from amorphous layers. Here, narrow temperature widths are explained in terms of normal gas motion within a confined region. In the present work the confined region would presumably be that in which the density of trapping sites is high, and its existence has experimental precedence in work by the authors on gas motion in metals[25]. The main weakness of this model is in understanding why gas should tend to remain in a confined region.

Although there are indications that trapping is a steady function of dose, the data of Fig. 5 imply that there are either two distinct separate processes or else that there are two limits of these processes: pure ideal volume diffusion and trapping. A similar conclusion has recently been reached for the system Kr/Xe – KCl[9].

As seen in Fig. 3, doping (adding $CaCl_2$ impurities) did not appreciably affect the results. This indicates that an increased concentrations of cation vacancies (decrease in concentration of anion vacancies) does not affect trapping appreciably. In addition, this result shows that NaCl does not behave like KBr[8], UO_2[28], or ThO_2[29] where doping *did* affect trapping.

Summary

The present study provides extensive data on the mobility (diffusion and trapping) of the *heavy* rare gases Kr, Xe, and Rn in NaCl and provides some new insigths into the release mechanisms at high doses. The main results can be summarized as follows:

1) At low gas concentrations, the release is compatible with volume diffusion and follows approximately theoretical expectations and empirical rules. The activation enthalpy, ΔH, is 1.5 ± 0.2 eV. Doping does *not* appreciably affect the release. A mobility in small vacancy clusters (e. g. divacancies) is suggested for the release mechanism.

2) At high concentrations, trapping (i. e. gas-gas or gas-damage interactions) occurs. By using high

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bombardment energies (up to 500 keV), it is shown that the final retarded release of trapped gas has a partially single jump character: The temperature interval of release and (sometimes) its dependence on bombardment energy are too small for an ideal volume diffusion process, but are still too large for a pure single jump process.

Acknowledgements

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Mischungseffekte binärer Systeme aus Benzol und einigen seiner Quasi-Dimeren

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Herrn Prof. Dr. G. KORTÜM *zum 65. Geburtstag gewidmet*

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Es wird gezeigt, daß experimentelle Daten von Exzeßgrößen bei +35 °C der Systeme Benzol—o,o′-Ditolyl, Benzol—Diphenylmethan und Diphenylmethan—o,o′-Ditolyl durch Ansätze der Theorie des Durchschnittspotentials unter alleiniger Berücksichtigung der Größenunterschiede der Moleküle gut wiedergegeben werden können. Dagegen ergeben sich beim System Benzol—Diphenyl Diskrepanzen.

KORTÜM und Mitarbeiter haben die Theorie der athermischen Mischungen [1, 2] und die von GUGGENHEIM und Mitarbeitern [3] erweiterte Theorie der streng regulären Lösungen auf die Systeme Benzol-Diphenyl [4] und Benzol-o,o′-Ditolyl [5, 6] angewandt und die theoretischen mit experimentellen Ergebnissen verglichen.

In einer weiteren Arbeit [7] wurden die Aussagen des von PRIGOGINE und Mitarbeitern [8] ausgearbeiteten Modells des Durchschnittspotentials an den Mischungen von Benzol mit seinen Quasidimeren Diphenyl, o,o′-Dilotyl und Diphenylmethan geprüft. Die Ursache der dabei gefundenen Abweichungen der theoretischen von den experimentellen Werten konnte nicht geklärt werden, da in die Prigogineschen Ansätze eine Reihe nicht genau bestimmbarer Parameter eingeht.

Beim dimer-dimer-System Diphenylmethan-o,o′-Ditolyl werden die Mischungseffekte im wesentlichen durch den Parameter ϱ, der die Größenunterschiede der Moleküle ausdrückt, bestimmt. Wir haben daher die mittlere molare Mischungswärme dieses Systems bei +35 °C gemessen und wollen damit die Aussagen des Prigogineschen Modells vergleichen.

Herstellung und Reinigung der Substanzen

o,o′-Ditolyl stellten wir aus o-Jodtoluol her. o-Jodtoluol wurde durch Diazotieren von o-Toluidin und anschließendem Verkochen mit Kaliumjodid erhalten [8a]. Zur Abspaltung des Jod und zur Koppelung des Tolyls zum o,o′-Ditolyl ließen wir das o-Jodtoluol bei einer Reaktionstemperatur von 180 bis 200 °C auf „Naturkupfer“ C tropfen. Dabei muß das als Nebenprodukt gebildete Toluol durch einen seitlichen Ansatz laufend abdestilliert werden, da sonst diese hohe Reaktionstemperatur nicht erreicht wird.

Die Reinigung des Endproduktes geschah durch Vakuumdestillation an einer kleinen Rektifiziersäule und durch mehrfaches Umkristallisieren.

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