Cell nr.	T_C (°K)	T_H (°K)	$(Q-1)\cdot 10^2$	$\alpha\cdot 10^2$	φ_{min}
I	438±5	805±8	1.20±0.25	2.03±0.42	5.4±1.1
II	438±5	788±8	1.20±0.23	2.10±0.40	5.5±1.1
III	437±5	754±8	1.12±0.21	2.10±0.40	5.4±1.1
IV	437±5	692±8	0.81±0.20	1.87±0.46	4.4±1.2

Table 1. Separation factors, thermal diffusion factors, cluster parameters.

Metal	Ref.	ψ_{max} (%)
Li	[1]	10.4
K	[3]	12.5
Rb	[3]	10.0
Ga	[2]	4.9
In	This work	9.7

Table 2. Theoretically estimated relation of displacement length to cluster diameter.

$$\varphi(E_m - E_f) = -20(M/\Delta M)\,\frac{Q-1}{T_C^{-1}-T_H^{-1}}\,. \qquad (1)$$

Here E_f is the energy of void formation and E_m of diffusive motion. M and ΔM denote atomic mass and the isotopic mass difference, respectively. The factor φ expresses the ratio of the effective radius of the diffusing species (an atom or a "cluster") to the mean diffusive displacement length. E_m is probably much smaller than E_f. Neglecting E_m, and thus substituting the entire "activation energy" E_D of diffusion for the energy difference on LHS of Eq. (1), is thus a reasonable approximation and at any rate gives a minimum limit of φ. When computing φ_{min} in Table 1, the experimental value $Q_D = 2430$ cal/mole was used [6]. The result, $\varphi_{min} = 5.15 \pm 0.45$, is in qualitative agreement with the results for other metals. This is shown in Table 2, where the obtained values of $\psi_{max} = 100/2\,\varphi_{min}$, i. e. the mean displacements in percent of cluster diameters, are compared.

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Diffusion of Sodium in Lithium

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The diffusion of ^{22}Na in solid lithium has been measured between 50 and 176 °C. The data fit the Arrhenius relation $D = D_0 \exp(-Q/RT)$, where $D_0 = (0.41 \pm 0.09)$ cm² sec^{-1} and $Q = (12.61 \pm 0.15)$ kcal mol^{-1}. Similarities with other alkali metal diffusion data allow the conclusion that diffusion is by a vacancy mechanism.

A number of theories of impurity diffusion have been proposed, the most successful of which is based on a screened interaction model. This theory, proposed by Lazarus [1] and further developed by LeClaire [2], has accounted particularly well for impurity diffusion in metals with close packed structure. In b.c.c. metals the same success has not been achieved. While much of the data on such metals refer to the transition metals, for which the screened interaction model is unsatisfactory, the theory proved similarly unsuccessful in accounting for the alkali metal diffusion data of Barr, Mundy and Smith [3]. In order to carry out a further check of the theory we have measured the diffusion of ^{22}Na in lithium.

Experimental Method

The method used was to observe the diffusion out of a thin layer of radioactive ^{22}Na by sectioning. The techniques are essentially the same as those used by Mundy, Barr and Smith [4]. The ^{22}Na was prepared by means of ion exchange from $^{22}NaCl$ obtained from R.C.C. Amersham. The lithium (3N8) was obtained from Foote Comp., and cleaned by forcing the molten lithium through a stainless steel sinter (pore size ~ 25 μ). The lithium specimen was cast into a microtome holder and slowly cooled in order to obtain a large grain size (~5 mm diameter). The thin surface layer was made by vacuum evaporation. The diffusion anneals were carried out in an oil bath controlled to ±0.05 °C. A chromel-alumel thermocouple was used to record the temperature continuously and the plot was used to calculate the "warm up" and "quench" time corrections. The specimens were sectioned using a hand microtome and the section thickness determined by weighing. Allowance was made for the thermal expansion of the lithium at the anneal temperature using data from the American Institute of Physics Handbook. The ^{22}Na activity was determined using a NaI(Tl) well type scintillation counter and standard counting equipment.

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T °C	D cm² sec^{-1}
52.8	$(1.356 \pm 0.017) \times 10^{-9}$
69.8	$(3.814 \pm 0.081) \times 10^{-9}$
88.7	$(1.036 \pm 0.014) \times 10^{-8}$
112.5	$(2.979 \pm 0.028) \times 10^{-8}$
130.3	$(5.491 \pm 0.364) \times 10^{-8}$
155.2	$(1.445 \pm 0.046) \times 10^{-7}$
175.9	$(3.070 \pm 0.067) \times 10^{-7}$

Table 1. Experimental results.

Element	D_0 (cm² sec^{-1})	Q (kcal mol^{-1})	T_m (°K)	Q/T_m	Method	Reference
Li	0.41	13.47	459.2	29.3	Diffusion Couple	5
	—	13.2	459.2	28.8	NMR	7
	—	12.00	459.2	26.2	NMR	8
	—	11.88	459.2	25.7	NMR	9
Na	0.145	10.09	371.0	27.2	Tracer Diffusion	4
K	0.31	9.75	336.9	28.9	Tracer Diffusion	6

Table 2. Hitherto obtained self-diffusion data in the alkali metals.

Experimental Results

The penetration profiles which were measured over a range of 20 in activity were linear if the initial point was rejected. The initial point was invariably high, due to oxide hold-up. The experimental values of the diffusion coefficient, D, are given in Table 1 and plotted in Fig. 1. The errors in D are individually quoted, as the major errors arose from the scatter in the penetration profiles and this varied from run to run. The data were fitted by a least squares method to the ARRHENIUS relation, $D = D_0 \exp(-Q/RT)$. The values of D_0 and the activation energy, Q, are given in Table 3. Also shown in Fig. 1 is the straight line obtained by a least squares fit of the data of NAUMOV and RYSKIN [5] for self diffusion in lithium. We found that their data yielded an activation energy of (13.475 ± 0.170) kcal mol^{-1} which is slightly lower than their quoted value of (13.49 ± 0.07) kcal mol^{-1}.

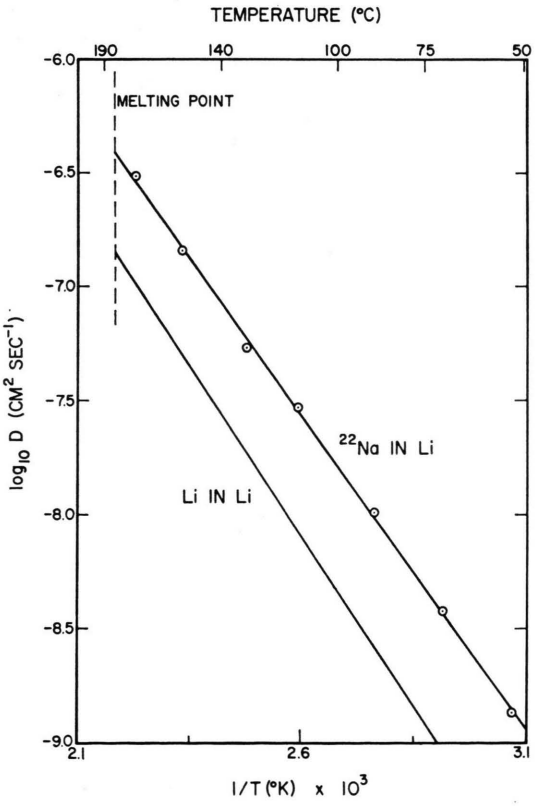

Fig. 1. Plot of $\mathrm{Log}_{10} D$ vs $1/T$.

Discussion

From the measurements of self diffusion in lithium [5], sodium [4] and potassium [6] it was concluded by the individual authors that diffusion occurred by means of a vacancy mechanism. A comparison of all the data is given in Table 2. While there is a certain amount of scatter, the correlation between the activation energies and the melting temperature, T_m, is good. This would indicate that self diffusion in the alkali metals is by the same mechanism. The isotope effect measurements in sodium [4] showed that the diffusion probably occurs by means of relaxed vacancies. In that the diffusion values of ^{22}Na in lithium lie within a factor of 5 of the self diffusion values it would seem reasonable to expect that the impurity diffusion is also by a relaxed vacancy mechanism.

The difference between the activation energies for impurity and self diffusion, δQ, can be estimated by LECLAIRE's theory [2]. The theory shows that the δQ for Na diffusion in Li should be of opposite sign and of similar size to the δQ for Li diffusion in Na. Measurements for the latter case have been made by NAUMOV [10] using a diffusion couple method and much higher concentrations of solute ($\sim 1\%$) than the present work. The diffusion coefficient measured is not a tracer diffusion coefficient, so the comparison made in Table 3 is not strictly valid. However, this is the only available data with which a comparison can be made.

It can be seen in Table 3 that the value of δQ for Na in Li depends on the value chosen for the self diffusion activation energy. The measurements of the activation energy for self diffusion in lithium tend to fall

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in two groups, one indicating a Q above 13 kcal mol^{-1}, the other $Q \approx 12$ kcal mol^{-1}. To try to clear up these differences we are measuring the self diffusion in lithium, using similar techniques as described above and analyzing with a mass spectrometer.

	D_0 (cm^2 sec^{-1})	Q (kcal mol^{-1})	δQ
Li in Na	1.8 ± 0.8	11.70 ± 0.20	$+1.61$
Na in Li	0.41 ± 0.09	12.61 ± 0.15	-0.86 to $+0.73$

Table 3. Comparison of present results with Li impurity diffusion in Na.

It should be noted that the average of the four values of Q(self) is 12.64 kcal mol^{-1} and this gives δQ equal to zero within experimental error. It is unfortunate that the discrepancies in these measurements make it difficult to make any real comparison with LeClaire's theory at the present time.

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Bemerkung zur Arbeit „Über die Kinetik der Wasserstoffpermeation durch Nickel"

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In einer vor kurzem in dieser Zeitschrift erschienenen Arbeit von Fischer [1] wird über die Messung des Durchtritts von Wasserstoff durch Nickelfolien unterschiedlicher Dicke zwischen 423 und 1000 °K berichtet. Für die Permeationsgeschwindigkeit (Mol $H_2 \cdot cm^{-1} \cdot s^{-1}$) unter den vom Autor gewählten Versuchsbedingungen (Wasserstoffdruck an der Eintrittsseite $p = 760$ Torr und $p \approx 0$ an der Austrittsseite) wird folgende Beziehung gefunden

$$P = 7{,}22 \cdot 10^{-7}/d \cdot \exp(-52\,400\ \mathrm{J \cdot Mol^{-1}}/RT), \quad (1)$$

mit der universellen Gaskonstanten $R = 8{,}314$ J · Mol^{-1} Grad^{-1}.

Unter Verwendung älterer Literaturangaben über die Löslichkeit von Wasserstoff in Nickel [2, 3] berechnet Fischer in seiner Arbeit mit Hilfe der Beziehung

$$P = D\,c/d \quad (2)$$

an Hand seiner gemessenen Permeationsdaten die Diffusionskoeffizienten von Wasserstoff in Nickel. In Gl. (2) bedeuten D den Diffusionskoeffizienten (cm$^2 \cdot$ s^{-1}), c die Konzentration des im Metall gelösten Wasserstoffs (Mol · cm^{-3}) bei einem Gleichgewichtsdruck von 760 Torr und d die Dicke der Membran (cm). Bei einem Vergleich der auf solche Weise erhaltenen Diffusionskoeffizienten mit bereits bekannten Daten wird u. a. Bezug genommen auf Meßwerte der Diffusion, die von mir früher veröffentlicht worden waren [4] und die, wie sich später herausstellte, wegen Verunreinigungen des Nickels ungenau waren. Es ist deshalb einzusehen, daß erhebliche Unterschiede zwischen diesen Werten und den von Fischer errechneten Daten (siehe Abb. 4 der zur Diskussion stehenden Arbeit) bestehen.

Wir haben etwas später ausführliche Untersuchungen über die Diffusion und die Löslichkeit von Wasserstoff und Deuterium in einem Nickel-Einkristall [5, 6] hoher Reinheit zwischen 633 und 933 °K ausgeführt. Die dabei angewandte Methode beruht auf der Beobachtung des zeitlichen Verlaufs der Entgasung von Metallkörpern geeigneter Gestalt (Kugel, Zylinder), für die die Diffusionsgleichung bequem zu lösen ist. Da dieses Verfahren gleichzeitig Diffusions- und Löslichkeitskoeffizient liefert, lassen die von uns veröffentlichten Daten unmittelbar und ohne Hinzunahme der Löslichkeitswerte Dritter einen Vergleich mit den von Fischer ausgeführten Permeationsmessungen zu.

Rechnet man die von uns gefundenen Temperaturfunktionen in die von Fischer benutzten Energieeinheiten um, so erhält man

a) für den Diffusionskoeffizienten

$$D = 6{,}73 \cdot 10^{-3} \cdot \exp(-39\,630\ \mathrm{J \cdot Mol^{-1}}/RT) \quad (3)$$

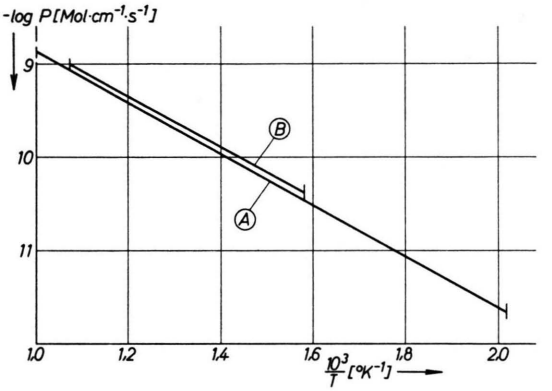

Abb. 1. Dekadischer Logarithmus der Permeationsgeschwindigkeit von Wasserstoff durch Nickel in Abhängigkeit von der reziproken absoluten Temperatur . A Messungen von Fischer. B Berechnet aus den Diffusions- und Löslichkeitskoeffizienten von Eichenauer, Löser und Witte. Die senkrechten Striche begrenzen den jeweiligen Meßbereich.

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