des Rohrstückes bis zum Loch, b der äußere Luftdruck, g die Erdbeschleunigung und p der Druck des Gases in der Apparatur. Der Schwingkörper befände sich in der Gleichgewichtslage, wenn

$$p = b + 4\, m_1\, g/\pi\, D^2 .$$

Schwingt der Schwingkörper um die Strecke x über die Gleichgewichtslage hinaus, wobei p sich um Δp ändert, so gilt

$$m_1\, \mathrm{d}^2x/\mathrm{d}t^2 = \tfrac{1}{4}\, \pi\, D^2\, \Delta p .$$

Der Vorgang ist adiabatisch, und aus $p \cdot V^{\varkappa} = \text{const}$ folgt

$$\Delta p = -\varkappa\, p\, \Delta V/V = -\frac{\varkappa\, p\, \pi\, D^2}{4\, V} \cdot x ,$$

also

$$m_1 \frac{\mathrm{d}^2x}{\mathrm{d}t^2} + \frac{\varkappa\, p\, \pi^2\, D^4}{16\, V} \cdot x = 0 .$$

Für die Kreisfrequenz ω dieser Schwingung gilt

$$\omega^2 = \frac{4\,\pi^2}{T^2} = \frac{\varkappa\, p\, \pi^2\, D^4}{16\, V\, m_1} .$$

Da leicht tausend Schwingungen gemessen werden können, muß noch eine Korrektion berücksichtigt werden, um die Genauigkeit voll auszunutzen. Die Gasmasse m_2 in dem Präzisionsglasrohr macht die Beschleunigungen des Schwingkörpers mit, an die Stelle von m_1 ist also zu setzen:

$$m = m_1 + m_2 .$$

Damit wird

$$\varkappa = 64\, m\, V/D^4\, p\, T^2 .$$

Bei einem von mehreren Geräten, die 1 Jahr einwandfrei im Praktikum arbeiteten, waren z. B.:

$$V = 2185\ \mathrm{cm}^3; \quad m_1 = 5{,}548\ \mathrm{g}; \quad m_2 = 0{,}031\ \mathrm{g}; \quad D = 13{,}93\ \mathrm{mm}.$$

Die Bestimmung der Schwingungsdauer wurde mit einer Lichtschranke vorgenommen und ergab bei Zählung von etwa 4000 Schwingungen je Meßpunkt:

Luft: $T = (385{,}35 \pm 0{,}05)$ ms, $\varkappa = 1{,}404 \pm 0{,}002$,
Argon: $T = (352{,}86 \pm 0{,}05)$ ms, $\varkappa = 1{,}659 \pm 0{,}002$,
CO_2: $T = (400{,}70 \pm 0{,}05)$ ms, $\varkappa = 1{,}300 \pm 0{,}002$.

Verwendet wurden Preßluft und technische Gase aus Stahlflaschen. Einige technische Einzelheiten seien noch erwähnt. Für gutes Funktionieren muß die Drosselstelle möglichst nahe am Glaskolben sein, und zum guten Durchspülen beim Gaswechsel wird der Gasstrom zweckmäßig bis zum Kolbenboden geleitet. Das Präzisionsglasrohr kann natürlich auch länger gewählt werden, z. B. 500 mm. Dann wird der Apparat für Praktikumszwecke ansehnlicher, aber die Meßwerte für $\varkappa$ werden dann um bis zu 0,5% kleiner, vermutlich wegen schlechter Adiabasie des Gases im Rohr selbst.

Als Material für den Schwingkörper hat sich nur PVC (Polyvinylchlorid) bewährt, alle anderen Materialien zeigten nach einigen 100 Schwingungen starke elektrische Aufladungen. Ferner war es nötig, das Präzisionsglasrohr mit 3-proz. Calciumchlorid-Lösung antistatisch vorzubehandeln und auch den PVC-Schwingkörper durch Einreiben mit Galvanographit oberflächlich zu graphitieren und damit elektrisch leitend zu machen.

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Diffusion of Tracer Indium in Liquid Gallium

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Impurity diffusion of ^{115m}In in liquid Ga has been investigated between 73° and 266 °C by a method earlier used for Ga self-diffusion. The results can be expressed by

$$D = 1.51 \cdot 10^{-3} \exp\{-1.32/R\,T\}\ (\mathrm{cm}^2/\mathrm{sec}).$$

The effective activation energy is only about 70% of that of self-diffusion. At the melting point of gallium the impurity- and self-diffusivity are about equal, but at the upper end of the range the tracer diffuses by about 40% slower than the host. The results can be reconciled with electrostatic screening arguments.

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We have utilized the main features of a method developed by Larsson et al. [1, 2] in an investigation of the diffusion of ^{115}In in liquid Ga. The method when earlier applied ot Ga self-diffusion [1] was "non-destructive"; the radioactive profile was studied by moving the metal column across a collimator slit. In the present case, in order to reduce the radioactivity required, the column was sectioned before counting. A correction for cooling contraction had to be made [3]. It had been demonstrated by test experiments on Ga self-diffusion [4] that the reproducibility of the sectioning method is of the order of 6%, as compared to about 2% of the "non-destructive" method. In all other respects the present experimental procedure was identical with that described in Ref. [1].

The results are plotted in Fig. 1 in an Arrhenius representation and compared with the self-diffusion results of Ref. [1]. A least squares treatment of the experimental points yields

$$D = 1.51 \cdot 10^{-3} \exp\{-(1.32 \pm 0.07)/R\,T\}\ (\mathrm{cm}^2/\mathrm{sec})$$

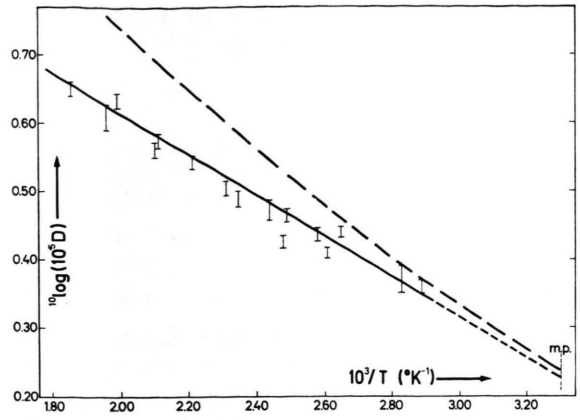

Fig. 1. Arrhenius plot of impurity diffusion of ^{115m}In in liquid gallium. Dashed curve: Ga self-diffusion, Ref. [1].

(energy in kcal/mole) for the diffusion of tracer In in liquid Ga between 73° and 266 °C.

The effective "activation energy", 1.32 kcal/mole, is by about 0.6 kcal/mole lower than that for Ga self-diffusion in the same temperature range. The two Arrhenius plots are seen to converge and cross not far from the melting point of Ga. The marked departure from a straight line, exhibited by the self-diffusion data [2], is also suggested by the present results.

At higher temperature the ratio of self-diffusion to tracer diffusion is about 1.4, i. e. significantly higher than the root of the ratio, 1.6, of the tracer masses.

Only few investigations have hitherto been made of impurity diffusion in liquid metals. In the Ag matrix system, LEAK and SWALIN [5, 6] have found a nearly linear dependence of ΔQ (= the difference in "activation energy" between solute and solvent diffusion) on the excess valence ΔZ of the impurity. The homovalent impurity Au in Ag, which according to LECLAIRE [7] possesses an effective ΔZ of about -0.9, has been found by GUPTA [6] to fit into the same systematics, $\Delta Q = -A \cdot \Delta Z$, where $A \cong 0.8$ kcal/mole. This is in agreement with arguments analogous to solid-state theory of impurity diffusion [7, 8], i. e. with the view that positive centers of charge should attract "free volume", as they attract vacancies in the solid metals. The analogy can be applied without giving preference to any particular model of liquid diffusion [6]. For the Ga matrix system, a similar treatment allows the qualitative prediction $A \approx 0.7$. Also according to Ref. [7], the excesss valency can be calculated for a homovalent impurity from

$$\Delta Z = \left[\Delta F + \frac{1}{n}\Delta H + \frac{1}{n}\Delta \Sigma I\right] B ,$$

where the RHS denotes the solute-solvent difference in Fermi energy, in the heat of sublimation and in the sum of the n ionization potentials. The factor B is of the order $1.6 \cdot 10^{-2}$; for In in Ga $n = 3$ and the parenthesis is about 60. Accordingly $\Delta Z \cong +1.0$, i. e. the In tracer in Ga behaves as effectively tetravalent. The analogy with the treatment of Ag-data [6] then leads to the prediction $\Delta Q \cong -0.7$, in good qualitative agreement with the observed $\Delta Q_{\text{exp}} \cong -0.6$.

In spite of the smaller "activation energy", the ratio D_i/D_s (i for impurity-, s for self-diffusion) is less than unity throughout the range. Perhaps this may be connected with the great difference in mass between solute and solvent. However, the oposite behaviour is reported for Au in Ag; the heavy solute has the greater "activation energy" but diffuses faster than the solvent. A common feature for both cases is that D_i/D_s is nearly unity at the melting point. Similar tendencies are seen in recent [9] measurements of the diffusion of ^{24}Na in K and ^{42}K in Na. The melting point cross-over may possibly be a clue to a further elaboration of liquid diffusion theory.

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Vibrational Spectra and Force Constants of the Ions $^{92}MoO_4^{2-}$, $^{100}MoO_4^{2-}$, $^{92}MoS_4^{2-}$ and $^{100}MoS_4^{2-}$

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In the course of our systematic investigations of the spectroscopic properties of tetrahedral oxo-, thio- and seleno anions of transition metals with d^0 configuration, we have studied the internal vibrations of MoO_4^{2-} and MoS_4^{2-} from the infrared and Raman spectra of the salts Na_2MoO_4 and K_2MoS_4. It seemed to be interesting to see whether it is possible to calculate the exact values of the force constants using very heavy atom isotopic substitution data, because until now this problem has not been investigated.

The well known compounds were prepared on a milligram scale using the metal isotopes purchased from Oak Ridge National Laboratory. The purity of each metal isotope was: ^{92}Mo (98.27%) and ^{100}Mo (97.42%). The infrared spectra were measured