The investigation of more families of systems containing hydrocarbons is in progress.

Acknowledgments

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. The apparatus was partially built with the financial aid of the Consiglio Nazionale delle Ricerche (Rome).

Miscibility Gaps in Fused Salts

Note III. Systems of Mercury Halides with Alkali Nitrates *

Cesare Sinistri, Giorgio Flor, Paolo Franzosini, and Mario Rolla

Institute of Physical Chemistry, University of Pavia, Italy

(Z. Naturforschg. **22 a**, 53—58 [1967]; received 1 October 1966)

Molten mixtures of $HgCl_2$, $HgBr_2$ and HgJ_2 with alkali nitrates have been investigated. Two liquids regions occur in the following systems: $HgCl_2$ + (Li, Na) NO_3, $HgBr_2$ + (Li, Na, K, Rb) NO_3 and HgJ_2 + (Li, Na, K, Rb, Cs) NO_3. The ability of demixing progressively increases in the sense Cs → Li and Cl → J. Moreover the composition squares of the systems Na, Hg/NO_3, Cl and (Na, K, Rb), Hg/NO_3, Br have been partially drawn.

Following our previous work on liquid-liquid (LL) equilibria in molten salt mixtures, in the present paper we have investigated the occurrence of demixing in type Me, Hg/NO_3, X systems, where Me = Li, Na, K, Rb, Cs and X = Cl, Br, J.

Little is known in literature about such systems, which are formed by salts predominantly covalent mixed with salts predominantly ionic. Bergman [1] has studied the behaviour of some mixtures of HgJ_2 with (Li, Na, K) NO_3. He found that the solubility of the first salt is particularly low in molten lithium nitrate. More recently Guenther [2] has performed distribution experiments between the two immiscible salt phases in the system $HgBr_2 + LiNO_3$ at 254 °C.

Apparatus and Materials

The apparatus used is the same already described in Note I [3]: however it has been found expedient to keep the Pyrex test-vessels immersed in a fused salt bath, rather than in an air bath.

All chemicals used (C. Erba, Merck or Light) were of reagent grade purity and were carefully dried before use.

Results and Discussion

a) $MeNO_3 + HgX_2$ mixtures. In Fig. 1 the LL and SL (solid-liquid) curves of 15 mixtures $MeNO_3 + HgX_2$ are shown. They are principal diagonal sections in the composition squares of the corresponding Me, Hg/NO_3, X systems. In Fig. 1 the empty circles represent experimental data, the filled ones extrapolated data (in the way specified later on). The areas in which LL equilibria occur are dashed.

As regards mercury chloride, demixing occurs in the mixtures with lithium and sodium nitrate, the extent of the miscibility gap (MG) being larger in the first case. In the mixtures with potassium, rubidium, and caesium nitrates a eutectic and, respectively, the congruent compounds $(RbNO_3)_2 \cdot HgCl_2$ and $CsNO_3 \cdot HgCl_2$ are formed.

As regards mercury bromide, demixing occurs with lithium, sodium, potassium, and rubidium nitrates, the MG being the largest in the case of $LiNO_3$. In the $CsNO_3 + HgBr_2$ system the formation of a eutectic occurs.

Finally, as regards mercury iodide demixing occurs with all the five alkali nitrates.

* Work carried out with the financial aid of the Consiglio Nazionale delle Ricerche, Rome.

[1] A. G. Bergman, Z. Anorg. Chem. **157**, 83 [1926].

[2] K. F. Guenther, J. Inorg. Nucl. Chem. **27**, 1427 [1965].

[3] C. Sinistri, P. Franzosini, A. Timidei, and M. Rolla, Z. Naturforschg. **20 a**, 561 [1965].

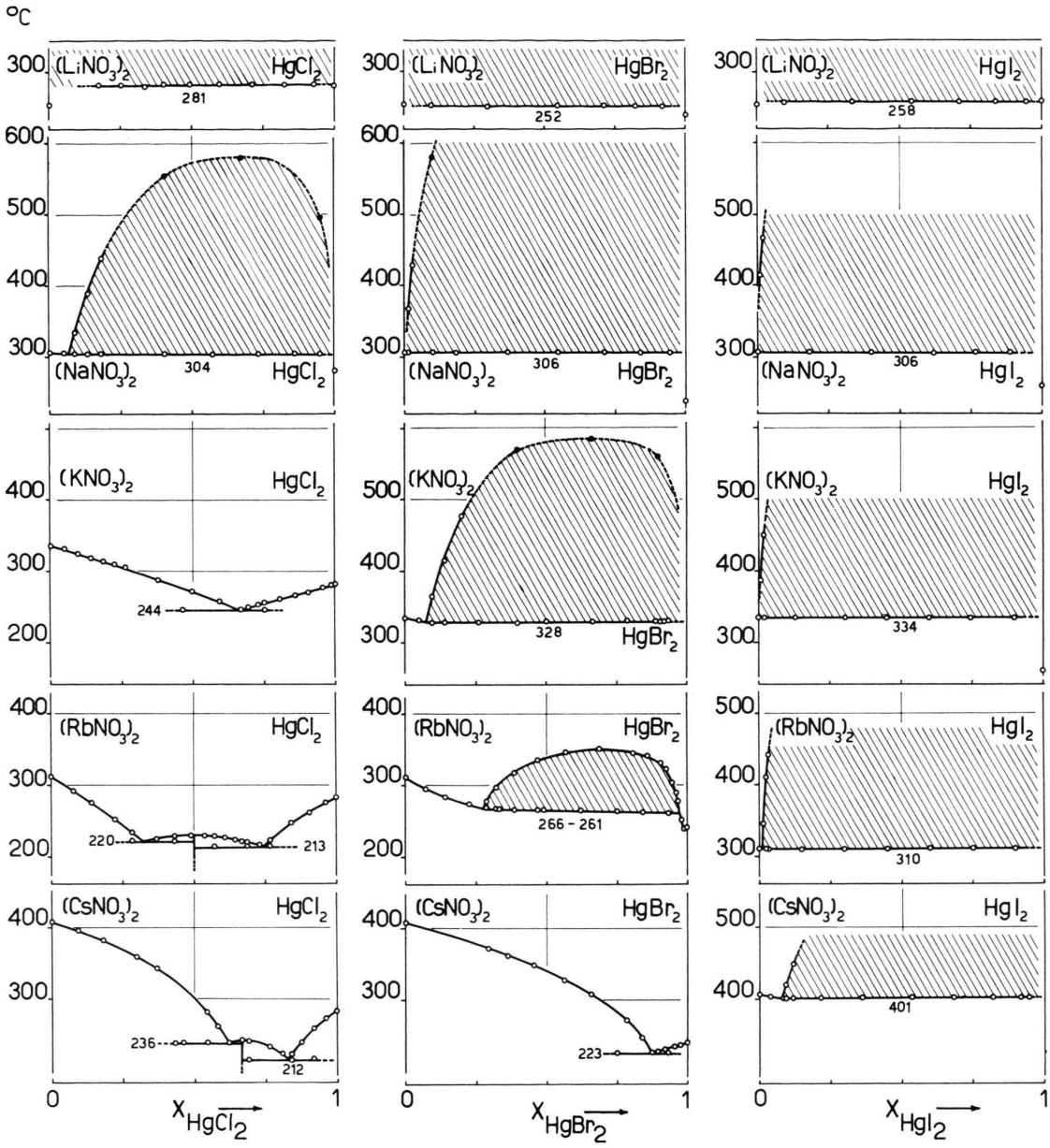

Fig. 1. Mixtures of mercuric chloride, bromide, jodide with alkali nitrates.

Because of the thermal instability of the components, it has been possible to measure the MG thoroughly only in the $RbNO_3 + HgBr_2$ system: the abscissa of the maximum, singled out by applying the CAILLETET–MATHIAS's rule, is $(x_{(RbNO3)2})_{max} = 0.30$, the corresponding ordinate being $t_{max} = 350$ °C.

The primary crystallization temperature (PCT) from one of the two liquid phases in equilibrium, generally remains constant within the experimental fluctuations: only for $RbNO_3 + HgBr_2$ mixtures, the PCT's diminish slightly and gradually, as the molecular fraction of the halide increases.

In Table 1 the principal features of the investigated systems are summarized: a qualitative evaluation of their ability of demixing (AOD) is also given.

	$HgCl_2$ m. p. 281 °C Ref.[4]	$HgBr_2$ m. p. 238.5 °C Ref.[5]	HgJ_2 m. p. 258 °C Ref.[4]
$LiNO_3$ m.p.253 °C Ref.[6]	Two liquid phases PCT = 281 °C AOD : very strong	Two liquid phases PCT = 252 °C AOD : very strong	Two liquid phases PCT = 258 °C AOD : very strong
$NaNO_3$ m.p.306 °C Ref.[6]	Two liquid phases PCT = 304 °C AOD : mean	Two liquid phases PCT = 306 °C AOD : strong	Two liquid phases PCT = 306 °C AOD : strong
KNO_3 m.p.334 °C Ref.[6]	One liquid phase Eutectic: $t_E = 244$ °C $x_{(KNO_3)_2} = 0.33_5$	Two liquid phases PCT = 328 °C AOD : mean	Two liquid phases PCT = 334 °C AOD : strong
$RbNO_3$ m.p.310 °C Ref.[7]	One liquid phase Eutectic: $t_E = 220$ °C $x_{(RbNO_3)_2} = 0.67_5$ Congruent compound $(RbNO_3)_2 \cdot HgCl_2$ m.p.228 °C Eutectic: $t_E = 213$ °C $x_{(RbNO_3)_2} = 0.26_5$	Two liquid phases PCT = 266–261 °C AOD : weak	Two liquid phases PCT = 310 °C AOD : strong
$CsNO_3$ m.p.406 °C Ref[8]	One liquid phase Eutectic: $t_E = 236$ °C $x_{(CsNO_3)_2} = 0.38$ Congruent compound $CsNO_3 \cdot HgCl_2$ m.p. 239 °C Eutectic: $t_E = 212$ °C $x_{(CsNO_3)_2} = 0.17$	One liquid phase Eutectic: $t_E = 223$ °C $x_{(CsNO_3)_2} = 0.13$	Two liquid phases PCT = 401 °C AOD : mean

Table 1. Type $MeNO_3 + HgX_2$ systems (Me=Li, Na, K, Rb, Cs; X=Cl, Br, J).

It may be pointed out that in the mixtures containing the same mercury halide the AOD increases as the radius of the alkali cation diminishes, whereas in those containing the same alkali nitrate the AOD increases when mercury chloride, bromide and iodide are successively taken as HgX_2. This is in agreement with what had previously been observed for the $MeNO_3 + TlX$ mixtures [3].

b) Offdiagonal cuts in the composition squares. In order to get a more complete information about the shape and extent of the two liquid phases regions, some offdiagonal cuts have been studied in the composition squares of the following systems.

System	*Cut*	*Starting mixture*	*Component added*
Na, Hg/NO_3, Cl		$(NaNO_3)_2 + HgCl_2$	$(NaCl)_2$
	A	4.5 : 1	
	B	1.5 : 1	
	C	1 : 2	
	D	1 : 18	
Na, Hg/NO_3, Br		$(NaNO_3)_2 + HgBr_2$	$(NaBr)_2$
	A	9 : 1	
	B	4 : 1	
	C	1.5 : 1	
	D	1 : 2	
	E	1 : 9	
K, Hg/NO_3, Br		$(KNO_3)_2 + HgBr_2$	$(KBr)_2$
	A	4 : 1	
	B	1.5 : 1	
	C	1 : 2	
	D	1 : 9	
Rb, Hg/NO_3, Br		$(RbNO_3)_2 + HgBr_2$	$(RbBr)_2$
	A	4 : 1	
	B	1.5 : 1	
	C	1 : 2	
	D	1 : 8	

Referring to the composition squares, all the cuts examined lie within triangles having the alkali nitrate and halide, and the mercury halide as vertices. It has not been possible to examine cuts lying within triangles having the mercury nitrate and halide, and the alkali nitrate as vertices, for $Hg(NO_3)_2$ samples of a satisfactory purity could not be prepared.

The results obtained are shown in Figs. 2 – 5, which are self-explanatory. In some cases, if a di-

[4] This work.
[5] G. J. Janz and J. Goodkin, J. Phys. Chem. **63**, 1975 [1959].
[6] P. Franzosini and C. Sinistri, Ric. Sci. **33** (II-A), 411 [1963].
[7] A. Mustajoki, Ann. Acad. Sci. Fennicae **A 6**, No. 9 [1958].
[8] A. Mustajoki, Ann. Acad. Sci. Fennicae **A 6**, No. 7 [1957].

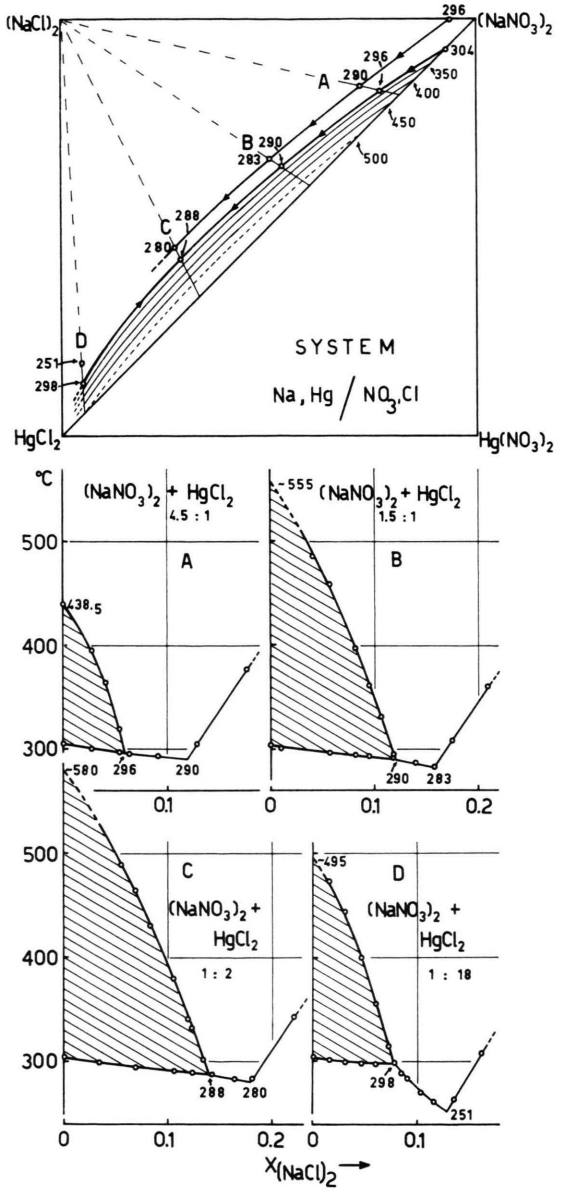

Fig. 2. Na, Hg/NO_3, Cl.

rect measurement has not been possible, approximate values of the consolute temperatures for such starting mixtures (zero amount of added component) could be obtained by extrapolation. These extrapolated values are shown in Fig. 1 as filled circles.

Moreover partial maps of the composition squares have been drawn. In these maps the projections of the non-isothermal curves delimitating the lenses of stratification, as well as those of the curves separating different crystallization fields are shown.

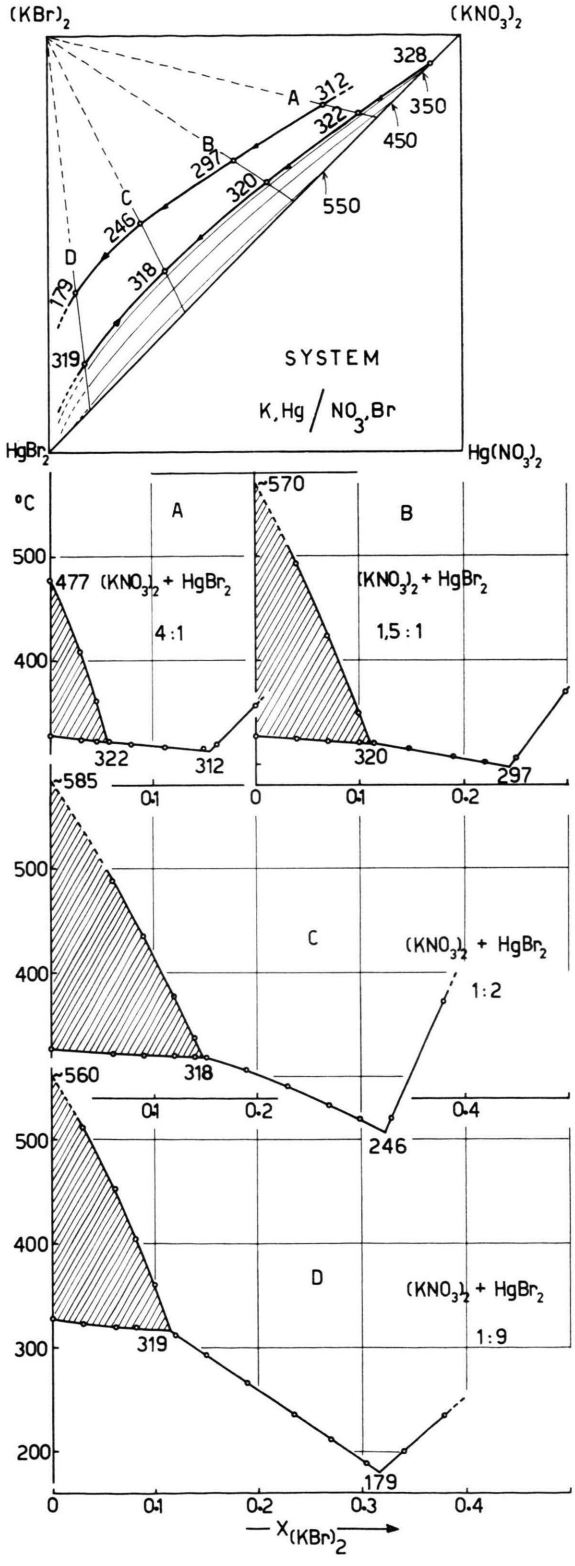

Fig. 4. K, Hg/NO_3, Br.

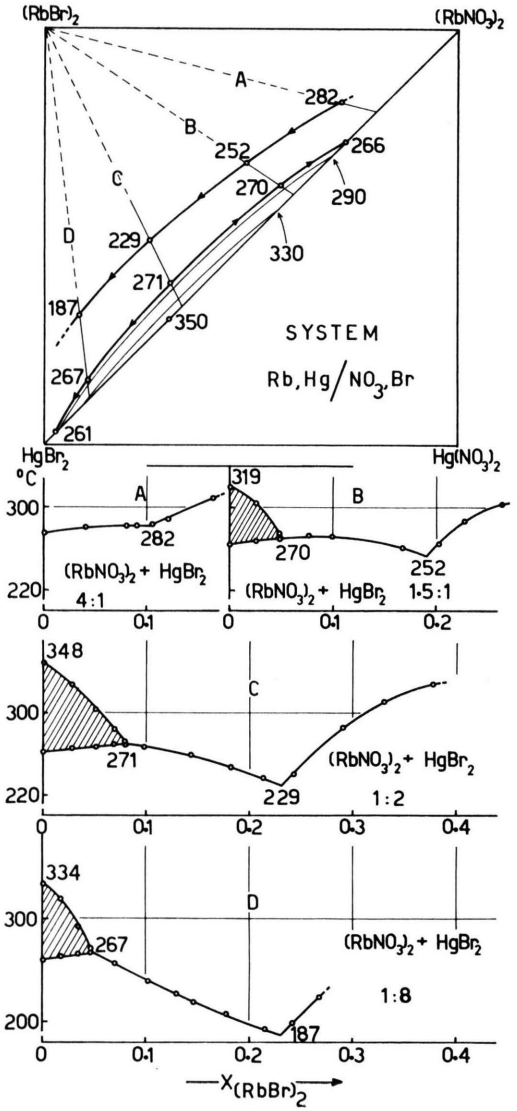

Fig. 5. Rb, Hg/NO_3, Br.

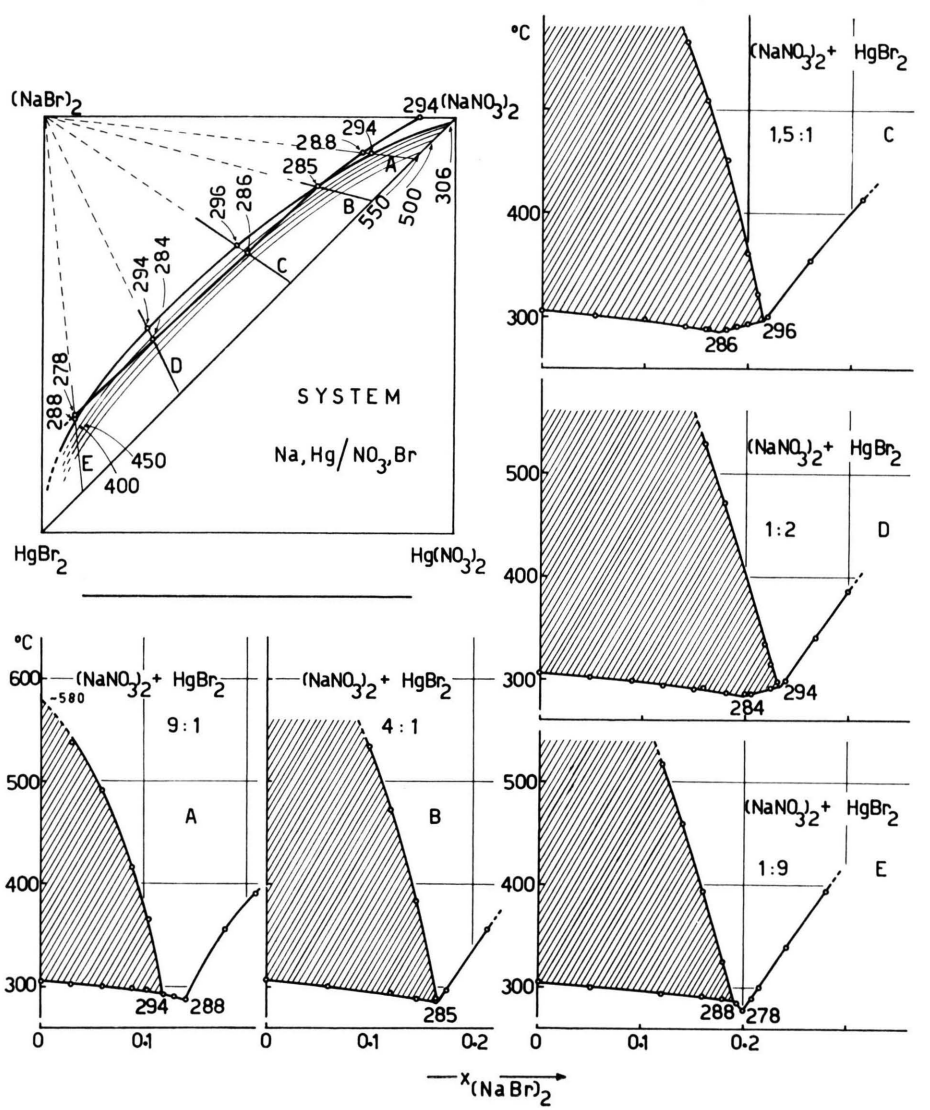

Fig. 3. Na, Hg/NO_3, Br.

The directions of the offdiagonal cuts and a certain number of LL isotherms are also drawn.

It is interesting that, at a certain temperature, the maximum observed transversal width of the MG becomes unusually small compared with the width of the two liquids region along the stable diagonal. Most probably this is to be put in connection with the formation of type HgX_{n+2}^{n-} complex ions in the melt, when increasing amounts of alkali halide MeX are progressively added to a starting mixture of $MeNO_3$ with HgX_2.

Der Diffusionskoeffizient des Nickels im flüssigen Kupfer

J. GERLACH und B. LEIDEL

Institut für Metallhüttenkunde der Technischen Universität Berlin

(Z. Naturforschg. **22 a**, 58—61 [1967]; eingegangen am 8. Oktober 1966)

Der Diffusionskoeffizient des Nickels im flüssigen Kupfer wurde zwischen 1150 und 1400 °C bei verschiedenen Konzentrationen mit der Kapillar-Reservoir-Methode ermittelt. Die Temperaturabhängigkeit der Diffusionskoeffizienten bei verschiedenen Konzentrationen beschreiben folgende Gleichungen:

0,025% Nickel: $D = (5{,}90 \pm 0{,}8) \cdot 10^{-3} \cdot \exp\{-(12960 \pm 1100)/RT\}$
0,25 % Nickel: $D = (2{,}31 \pm 0{,}35) \cdot 10^{-3} \cdot \exp\{-(7690 \pm 900)/RT\}$
2,5 % Nickel: $D = (1{,}79 \pm 0{,}15) \cdot 10^{-2} \cdot \exp\{-(9900 \pm 825)/RT\}$
3,25 % Nickel: $D = (5{,}81 \pm 0{,}45) \cdot 10^{-2} \cdot \exp\{-(12560 \pm 1000)/RT\}$

Nachdem in früheren Arbeiten die Diffusion des Sauerstoffs [1] und des Schwefels [2, 3] studiert worden war, kann nunmehr auch das Diffusionsverhalten des Nickels in flüssigem Kupfer mitgeteilt werden. Die Versuche wurden wie in [3] nach der Kapillare-Reservoir-Methode von ANDERSON und SADDINGTON [4] durchgeführt.

Versuchsanordnung und -durchführung

Es wurden Kapillaren aus reinem Sinterkorund verwendet, die einen Durchmesser von 1,3 – 1,5 mm hatten und 30 – 35 mm lang waren.

Um die Konzentrationsabhängigkeit des Diffusionskoeffizienten bestimmen zu können, wurden Legierungen mit verschiedenen Kapillar- und Reservoirkonzentrationen in einem Vakuum-Induktionsofen erschmolzen. Bis zu einem Gehalt von 0,5% Nickel geschah das in Graphittiegeln. Die Kohlenstoffaufnahme der Schmelzen war dabei nicht höher als der bekannte Wert für reines Kupfer [5]. Bei höheren Ni-Gehalten wurden Magnesittiegel benutzt.

Das Füllen der Kapillaren geschah in ähnlicher Weise wie bei der Bestimmung der Diffusionskoeffizienten des Sauerstoffs [1] und des Schwefels [2, 3] in Kupfer. Die dort beschriebene Versuchsapparatur wurde auch für die Versuche dieser Arbeit benutzt. Es wurden die Diffusionskoeffizienten in Abhängigkeit von der Temperatur in vier Meßreihen bestimmt. Die Konzentrationen in der Reservoirschmelze und in den Kapillaren vor den Versuchen sind in Tab. 1 aufgeführt.

In der Tabelle sind am Schluß außerdem die Konzentrationen von einigen Einzelversuchen angegeben, die nicht zur Bestimmung der Temperaturabhängigkeit herangezogen wurden.

Die Diffusionsversuche wurden zwischen 1150 und 1400 °C in Abständen von etwa 50 °C durchgeführt. Die Diffusionszeit betrug 10 bis 30 Minuten.

Versuchsauswertung

Um die Versuche auswerten zu können, mußte die Länge der Diffusionssäule bei Versuchstemperatur bestimmt werden. Die Diffusionssäule wird zuerst an der kältesten Stelle, an der Kapillarmündung, erstarren. Am geschlossenen Ende der Kapillare entsteht ein Schrumpfungslunker. Schleift man vorsichtig den Boden der Kapillare ab, so ist der Rest der Kapillare praktisch so lang wie die Diffusionssäule bei Versuchstemperatur l_1. Nach dem Zerschlagen der Kapillare erhält man die Länge bei Raumtemperatur l_0. Das Verhältnis der beiden Längen ergibt einen Kor-

[1] H. G. KLEIST, Dissertation, Technische Universität Berlin 1962.
[2] K. MAGER, Dissertation, Technische Universität Berlin 1963.
[3] J. GERLACH, H. G. KLEIST u. K. MAGER, Z. Naturforschg. **19 a**, 1486 [1964].
[4] J. S. ANDERSON u. K. SADDINGTON, J. Chem. Soc. **1949**, S 381 bis S 386.
[5] M. B. BEVER u. C. F. FLOE, Trans. AIME **166**, 128 [1946].