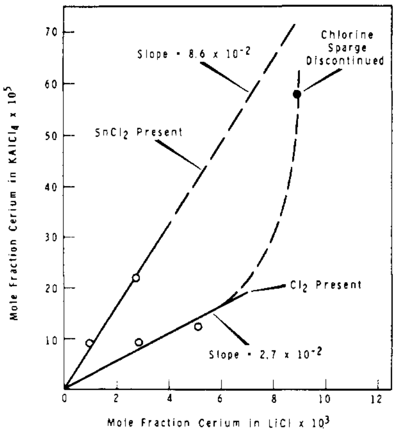

Figure 5. Distribution of cerium chloride at 625° C.

Table III. Distribution Coefficients for Metal Chlorides in the System: LiCl–KAlCl$_4$ at 625° C.

	Probable Species Distributing	K_D
UO_2Cl_2	$UO_2Cl_4^{-2}$	0.84
$UCl_4(+ SnCl_2)$	UCl_6^{-2}	1.62
UCl_3	UCl_3	0.04
$PuCl_4(+ Cl_2)$	$PuCl_6^{-2}$	1.9
$PuCl_3$	$PuCl_3$	0.04
$CeCl_3(+ Cl_2)$	$CeCl_6^{-2}$	0.03
$CeCl_3(+ SnCl_2)$	$CeCl_6^{-3}$	0.09
$FeCl_2$(+ UCl_3, excess)	$FeCl_4^{-2}$	0.75
$FeCl_3$	$FeCl_4^{-1}$	9.1
$RuCl_3$	$RuCl_6^{-3}$	0.24
$SnCl_2$	$SnCl_4^{-2}$	0.9
$SrCl_2$	Sr^{+2}	0.014
NaCl	Na^{+}	0.56
CsCl	Cs^{+}	18.1

was allowed to stand for 40 minutes with no chlorine sparge, and then samples were taken which yield the point shown as a solid circle and a distribution calculated to be 5.9×10^{-2}.

With $SnCl_2$ present, the distribution coefficient should be that due to $CeCl_3$, probably the $CeCl_6^{-3}$ complex anion. With chlorine present, oxidation to $CeCl_4$ would be anticipated, and since this is an unstable substance at a temperature of 625C, removal of the chlorine sparge should result in reversion to $CeCl_3$, as appeared to occur.

The $CeCl_6^{-3}$ complex ion is a larger anion than the $CeCl_6^{-2}$ complex ion and it exhibits a larger distribution coefficient as was expected for the trivalent complexes of uranium and plutonium. Evidently the $CeCl_6^{-3}$ complex ion is appreciably more stable than UCl_6^{-3} or $PuCl_6^{-3}$ and is formed at the chloride ion activity which prevails in this system.

The distribution data are summarized in Table III. In general, these data were obtained with the distributing species as the sole solute unless oxidizing or reducing agent was required, as indicated. There is no evidence that these data will hold for a given distributing solute in more complex mixtures. Consequently, the data are merely indicative of the results to be anticipated in a practical case. However, the data indicate that a number of separations of practical interest can be achieved.

LITERATURE CITED

(1) Katz, J.J., Rabinowitch, E., "The Chemistry of Uranium, Part I. The Element, Its Binary and Related Compounds," p. 583, McGraw-Hill, New York, 1951.
(2) Moore, R.H., J. Chem. Eng. Data 8, 164, (1963).
(3) Morrey, J.R., *Inorg. Chem.* 2, 163 (1963).
(4) Morrey, J.R., Private communication, General Electric Co., Richland, Wash., August 8, 1962.

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High-Temperature Heat Content of Niobium

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High-temperature heat contents of niobium were measured over the temperature range 298° to 1415° K., using a diphenyl ether calorimeter. Smoothed values of the thermal properties of niobium, $H_T^\circ - H_{298}^\circ$, C_p, $S_T^\circ - S_{298}^\circ$, and $(F_T^\circ - H_{298}^\circ)/T$, have been derived and are tabulated at even 100° intervals. Within an average deviation of 0.10%, the tabular heat content values are given by the expression:

$$H_T^\circ - H_{298.15}^\circ = 5.885T + 4.044 \times 10^{-4}T^2 + 2.194 \times 10^{4}T^{-1} - 1864.$$

GROWING INTEREST IN NIOBIUM as a high-temperature refractory metal plus the availability of a sample of high purity material have made it desirable to determine the high-temperature thermal properties of niobium by means of heat content measurements. Previously reported measurements of the high-temperature thermal properties of niobium by Jaeger and Veenstra (*5*) ($H_T^\circ - H_{295}^\circ$, 670° – 1828° K.), Lowenthal (*9*) (C_p, 1471° – 2259° K.), and Gel'd and Kusenko (*2*) ($H_T^\circ - H_{298}^\circ$, 433° – 1840° K.) are not in agreement. The data of the latter investigators, while recent and extensive, were reported for niobium containing 1.0% oxygen and 0.05% carbon. This paper reports the results of heat content measurements on pure niobium in the temperature range 298° to 1415° K.

EXPERIMENTAL

Electron-beam melted niobium supplied by the Temescal Metallurgical Corp. was used in the study. The stated maximum impurity levels indicate the sample to have a purity of 99.99+% Nb.

Heat content measurements were made using a diphenyl ether Bunsen-type drop calorimeter. The apparatus and

Table I. Experimental Results

(Niobium At. Wt. = 92.906)

T, ° K.	$H^\circ_T - H^\circ_{298.15}$ Cal./G. Atom	T, ° K.	$H^\circ_T - H^\circ_{298.15}$ Cal./G. Atom
358.3	350	813.2	3226
358.3	357	813.3	3216
397.6	594	892.2	3703
397.7	597	892.5	3729
440.2	858	892.5	3731
440.2	859	995.3	4416
502.2	1251	1002.5	4454
502.4	1239	1002.8	4472
502.4	1244	1006.0[a]	4500
585.7	1758	1006.2[a]	4521
586.0	1751	1102.9	5133
611.4	1919	1103.0	5139
611.4	1933	1203.2	5792
703.3	2515	1203.2	5821
703.4	2500	1302.9	6505
703.4	2502	1303.1	6518
715.0	2578	1414.5	7312
788.4	3039	1414.7	7348
788.5	3039		

[a] Runs made to confirm method of correcting for oxygen absorption (see text).

experimental procedures have been described in detail previously (*3*, *7*) and will be mentioned only briefly here. The specimen, consisting of 1.2795 grams of niobium enclosed in 0.5016 grams of platinum foil, was heated in an argon atmosphere in a vertical tube furnace to a measured temperature, then dropped into the calorimeter. Heat from the specimen entered a surrounding chamber containing liquid and solid diphenyl ether at its melting point, 300.0° K., melting some of the solid isothermally. The resulting increase in volume was measured by displacement of mercury from the bottom of the calorimeter chamber into a horizontal calibrated capillary tube. The heat effect was obtained from the measured volume change using the calibration factor determined by Jessup (*6*) and routinely checked throughout the measurements by dropping a solid platinum specimen in the calorimeter (*7*). Corrections were made for the heat content of the platinum capsule and the heat lost during the drop using data previously reported (*7*) and for the small difference between the calorimeter temperature, 300° K., and the standard reference temperature, 298.15° K., using the C_p at 298.15° K., selected by Hultgren and coworkers (*4*) from low-temperature data. Calculations were made using the 1961 International Atomic Weights (*1*).

Starting with the runs at 995° K. and continuing at higher temperatures, the specimen gained small amounts of weight due to oxygen absorption. The total increase in weight, reached after the highest temperature runs (1415° K.), was 0.0021 grams, amounting to 0.16% by weight. Correction was made for oxidation using the apparent heat content of oxygen in niobium, calculated from heat-content data for NbO_2 (*8*) and Nb_2O_5 (*10*). The corrections made varied from 0.3% to 1.0% of the measured values. After completion of the high-temperature runs, two final runs (indicated in Table I) were repeated at a lower temperature in order to check the method of correction. The results, after correction, were in good agreement with the values found before extensive oxidation had occurred.

Table II. Thermal Properties of Niobium

	Cal./Deg. Gram Atom			
T, ° K.	$H^\circ_T - H^\circ_{298.15}$ Cal./G. Atom	C_p	$S^\circ_T - S^\circ_{298.15}$	$\frac{F^\circ_T - H^\circ_{298.15}}{T}$
298.15	0	5.88	0.00	8.70
400	611	6.09	1.76	8.93
500	1226	6.18	3.13	9.38
600	1849	6.28	4.27	9.88
700	2482	6.38	5.24	10.40
800	3126	6.48	6.10	10.89
900	3778	6.58	6.87	11.37
1000	4442	6.68	7.57	11.83
1100	5116	6.79	8.21	12.26
1200	5799	6.88	8.81	12.67
1300	6493	6.99	9.36	13.06
1400	7196	7.09	9.88	13.44

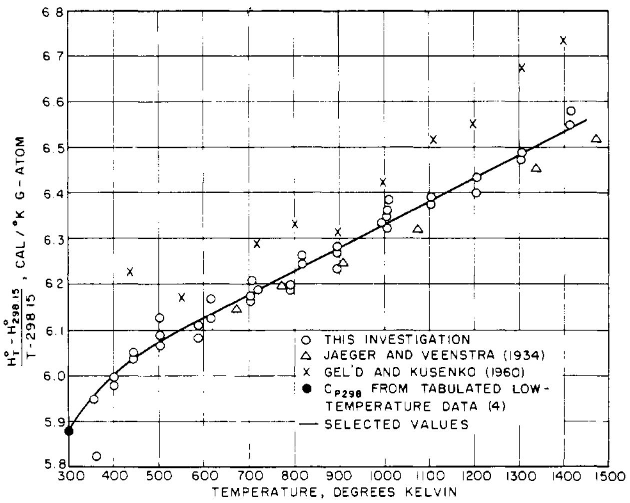

Figure 1. Heat content of niobium expressed in terms of the function $(H^\circ_T - H^\circ_{298.15})/(T - 298.15)$

RESULTS

The experimental results, after correction for oxygen absorption, are listed in Table I and are shown plotted in terms of the function $(H^\circ_T - H^\circ_{298.15})/(T - 298.15)$ in Figure 1. The selected curve joins smoothly in both C_p and (dC_p/dT) with the low-temperature C_p values selected by Hultgren and coworkers (*4*). The heat content values of Jaeger and Veenstra (*5*) are on the average about 0.5% lower than those found here, while those of Gel'd and Kusenko (*2*) are from 1% to 3% high. Heat capacity values of Lowenthal (*9*), determined from optical emission measurements on electrically heated filaments in the range 1471° - 2259° K., appear to be about 3% high. This tends to confirm Lowenthal's suspicion that his results may have been from 2.5% to 4% high due in part to uncertain knowledge of the optical emissivity of niobium (*9*).

Smoothed values of the thermal properties of niobium corresponding to the selected curve are tabulated in Table II. Values of the free energy function are based on $S^\circ_{298.15} = 8.70 \pm 0.1$ as given by Hultgren and coworkers (*4*). The tabulated heat content values are represented within an average deviation of 0.10% by the analytical expression:

$$H^\circ_T - H^\circ_{298.15} = 5885T + 4.044 \times 10^{-4}T^2 + 2.194 \times 10^4 T^{-1} - 1864$$

NOMENCLATURE

T = Temperature, ° K.
C_p = Heat capacity at constant pressure, cal./deg. gram atom
$S^\circ_{298.15}$ = Standard entropy at 298.15° K., cal./deg. gram atom
$H^\circ_T - H^\circ_{298.15}$ = Heat content (enthalpy) increment between 298.15° K., and temperature T, cal./gram atom
$S^\circ_T - S^\circ_{298.15}$ = Entropy increment between 298.15° K. and temperature T, cal./deg. gram atom
$(F^\circ_T - H^\circ_{298.15})/T$ = Free energy function with respect to 298.15° K., cal./deg. gram atom

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LITERATURE CITED

(1) Cameron, A.E., Wichers, E., *J. Am. Chem. Soc.* **84**, 4175 (1962).
(2) Gel'd, P.V., Kusenko, F.G., *Izv. Akad. Nauk SSSR, Otd. Tekhn. Nauk Met. i. Toplivo* **2**, 79 (1960).
(3) Hultgren, Ralph, Newcomb, Peter, Orr, Raymond L., Warner, Linda, Phys. Chem. Metallic Solns., Natl. Phys. Lab. Symposium No. 9, Vol. **I**, 1H, HMSO, London, 8 pp., 1959.
(4) Hultgren, Ralph, Orr, Raymond L., Anderson, P.D., Kelley, Kenneth K., "Selected Values of Thermodynamic Properties of Metals and Alloys," pp. 188–192, John Wiley, New York, 1963.
(5) Jaeger, F.M., Veenstra, W.A., *Rec. trav. Chim.* **53**, 677 (1934).
(6) Jessup, R.S., *J. Res. Nat. Bur. Std.* **55**, 317 (1955).
(7) Kendall, W.B., Orr, R.L., Hultgren, R., J. CHEM. ENG. DATA **7**, 516 (1962).
(8) King. E.G., Christensen, A.U., *U. S. Bur. Mines Rept. Invest.* **5789**, (1961).
(9) Lowenthal, G.C., *Australian J. Phys.* **16**, 47 (1963).
(10) Orr, R.L., *J. Am. Chem. Soc.* **75**, 2808 (1953).

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Phase Equilibria in the Potassium Hydroxide–Sodium Hydroxide System

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Equilibria in the potassium hydroxide–sodium hydroxide system have been investigated through observation of cooling curves. A eutectic point at 170° and 41 wt.% sodium hydroxide was found. Solid-solid transition temperatures for both components are lowered by the presence of the other. Solubility of NaOH up to about 10% in solid KOH and much smaller solubility of KOH in solid NaOH is indicated.

THE KOH-NaOH system has been investigated incidental to a project involving the use of the alkali hydroxides as solvents. The results are not in agreement with the phase diagram presented by Hevesy in 1910 (*2*). A more recent study by Reshetnikov and Unzhakov, as far as can be judged from a brief abstract (*3*), appears to agree with our findings but, in view of the inaccessibility of the Russian publication in which this work appears, it was thought desirable to present our phase diagram as deduced from cooling curves for various mixtures of the two components.

EXPERIMENTAL

The reagent grade potassium hydroxide employed was found by analysis to contain 14.8% water and 0.6% potassium carbonate while the sodium hydroxide initially was 0.6% water and 0.3% sodium carbonate. The potassium hydroxide was heated and held at 475–500° for 24 hours in a nickel container to remove water and the sodium hydroxide in an aluminum container was kept at 400° for 4–6 hours. The hydroxides as used contained 0.3 to 0.7% carbonate. It is estimated that the observed freezing points are 0.5 to 1.2° below what they would have been in the absence of carbonate. Although the fused samples were not completely protected from the atmosphere by dry nitrogen, molten samples could be kept for several days without absorbing enough water or carbon dioxide to cause a detectable change in their freezing points.

Aluminum cylinders holding about 50 grams total hydroxide were used for the cooling curve measurements. These cylinders were placed in an electric furnace to melt the hydroxides and regulate the rate of cooling. Cooling rates of about 1–2 deg./min. were used to ensure equilibrium conditions; no appreciable supercooling was observed. The tendency to creep up the walls is much less with aluminum than with nickel and the uncertainty of composition due to creep is minimized by its use. Nickel was required for the dehydration of the potassium hydroxide because its initially higher water content enables it to attack aluminum. When thoroughly dehydrated, however, no significant attack on aluminum is observed at temperatures lower than 450°.

Temperatures were measured by a chromel-alumel thermocouple which was calibrated with samples of tin, lead, and zinc whose freezing points had been certified by the National Bureau of Standards. Thermocouple EMF's were measured with a Leeds and Northrup type K-2 potentiometer and type E galvanometer. The thermocouple hot junction was immersed in the melt without protection, since there were no observable differences in the calibrated freezing points whether a protection tube was used or not.

RESULTS

Table I presents, for the various mixtures used, the temperatures at which breaks were observed in the cooling curves, interpreted as initial freezing, eutectic, and transition temperatures. These temperature-composition values are shown as points connected by the continuous lines in Figure 1. The dashed lines on the potassium hydroxide side refer to hypothetical equilibria involving solid solution and were not determined experimentally. A eutectic at 170° and 41% is clearly indicated, in contrast to the phase diagram of Hevesy (*2*) which shows continuous solid

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