composition, we thus obtain for the rate of evolution of oxygen the equation

$$dx/dt = kx(1 - x) + k_1(1 - x)^{2/3}$$

This equation was integrated numerically for a number of runs and found to coincide with the experimental curves. As the surface decomposition is as a rule much slower than the autocatalytic reaction, the fractional index may be taken equal to one to a good approximation; with $K = k_1/k$ integration gives

$$\frac{1}{K+1}\,[\log\,(K + x/1 - x) - \log K] = kt \qquad (1)$$

This equation offers two improvements as compared to that of Prout and Tompkins: (1) the plots of the logarithmic term *versus* time do not start at minus infinity; (2) by a proper choice of K the asymmetry of the sigmoid curve is compensated and a single rate constant is obtained.

From the inflection point of the experimental decomposition curves we have $K = 1 - 2x_{\max}$ ($x_{\max}$ being the fraction of solid decomposed up to the point of maximum reaction velocity). If K is extremely small, $x_{\max}$ is nearly equal to 50%,[6] and $k = k_a = k_d$. For medium values of K we have $k_a > k > k_d$. If K is large, equation (1) approaches the form of a first order kinetics (Fig. 7) and k approaches k_F. Also, when x is not very different from 1 a first order kinetics may be expected as quite frequently observed for the last part of the thermal decomposition of solids.[2]

In conclusion it seems reasonable to assume that in the various halogenide–perchlorate mixtures the governing factor is not the lowered melting point but the large increase in the number of perchlorate ions decomposed on the surface of the crystals because of the close contact with the halogenide ions (which is equivalent to a large increase in K). The values of k_a, A and E given in Tables I to IV are in accord with this hypothesis. For pure perchlorate these values differ only slightly from those of its mixtures with chloride. The main effect of the chloride is the shortening of the induction period. In the bromide mixtures a new ion is introduced which reduces appreciably the energy of activation and thereby produces a corresponding acceleration in the rate of reaction, without changing A significantly.

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[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS AND THE KNOLLS ATOMIC POWER LABORATORY]

Heat Capacity of Potassium and Three Potassium–Sodium Alloys between 0° and 800°, the Triple Point and Heat of Fusion of Potassium[1]

BY THOMAS B. DOUGLAS, ANNE F. BALL, DEFOE C. GINNINGS AND WILLIAM D. DAVIS[2]

Measurements were made of the changes in enthalpy of potassium and three potassium–sodium alloys (containing approximately 45, 54 and 78% of potassium) over the range 0 to 800°, using an ice calorimeter as earlier with sodium. The precision for two of the alloys was inferior to that usually obtained with this apparatus, owing to a solid-phase transformation during cooling. From the enthalpy values were derived the heat capacities, as well as the heat of fusion and relative entropy of potassium. The heat capacities of the liquid alloys were found to correspond closely at each temperature between 100 and 800° to those calculated additively from the authors' values for pure liquid potassium and sodium. As with sodium, each liquid shows a minimum in heat capacity between 500 and 650°. The melting curve and triple point of potassium also were determined.

It was the purpose of this investigation to measure accurately the heat capacities of potassium and three potassium–sodium alloys from 0° to approximately their normal boiling points. These measurements provided also an opportunity to study the deviations of the heat capacities of these alloys from those calculated additively from the values for the pure component elements. Because certain of these alloys have lower freezing points than pure sodium, it is sometimes more practical to use them as heat transfer media. Less precise measurements have been made by other observers on potassium up to about 350°, but no measurements seem to have been reported for any potassium–sodium alloy.

Experimental

Preparation of Samples.—Measurements were made on two samples each of 100%- and 78%-potassium and on one sample of each of the other two alloys. The samples were sealed in containers at the Knolls Atomic Power Laboratory. The containers were made from the same stock of stainless steel No. 347 as those used in the earlier investigation of sodium,[3] and had approximately the same size (about 10 cm.^{3}), shape and mass. Some modifications of the earlier procedure were necessary, owing to the greater chemical reactivity of the present materials.

The samples of 100% potassium were prepared by the triple distillation of a nominally pure sample from Baker Chemical Co. The three alloys, likewise having been prepared by distillation, were received in stainless steel cylinders from Mine Safety Appliance Co. One sample each of potassium and the 78% potassium alloy that had been used in the thermal measurements was analyzed spectrochemically at the National Bureau of Standards. Of the 55 chemical elements tested for, only the following were detected as impurities. In the sample of potassium were found between 0.01 and 0.1% of sodium, between 0.001 and 0.01% of calcium, and traces (less than 0.001% of each) of aluminium, chromium, iron, magnesium, rubidium, manganese and silicon. The 78% potassium alloy showed only calcium, magnesium, rubidium, iron and silicon, and these only in trace amounts.

The spectrochemical analysis did not include a search for the common non-metals. However, an analysis made

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(2) Knolls Atomic Power Laboratory, General Electric Company, Schenectady, New York.

(3) D. C. Ginnings, T. B. Douglas and Anne F. Ball, *J. Research Natl. Bur. Standards*, **45**, 23 (1950).

elsewhere of a sample of a potassium–sodium alloy that was believed to be typical of these, showed 0.009% of chlorine and 0.006% of sulfur, as well as 0.005% of calcium. The content of alkali-metal oxide was believed to be less than the saturation value of approximately 0.01%. Corroborative evidence as to the order of magnitude of the total impurity in the 100% potassium was provided by a melting curve described later.

The glass apparatus enclosing an empty sample container was designed to exclude all air and moisture. After a thorough evacuation and degassing by heating, it was filled and continually swept out with helium which had been purified by passing over hot calcium. The desired amount of either liquid potassium or one of these alloys was forced into the container by applying an excess pressure of helium to the supply container. At this time there was introduced into a side cavity of the apparatus a drop of a potassium–sodium liquid alloy, which served as a detector of any air or moisture that accidentally entered the apparatus during the filling and sealing process. The lid was next placed on the sample container by a rod moving through a softened wax joint. The lid was hammered into place by a small iron cylinder operated magnetically. After the pressure of helium was reduced to 2.5 cm. (absolute), the sample container was ready for welding on the lid. For this, a 50-kilowatt induction heater was used, the correct timing and power for the pulse having been previously determined experimentally. A preliminary test on two similar empty containers showed weight losses of less than one mg. each on welding.

After being welded, the containers were tested for tightness by being heated in vacuum for about ten minutes at 900°. No evolution of alkali metal could be detected. However, weight losses of as much as one mg. were observed, which were assumed to be due to evaporation of stainless steel and evolution of dissolved gases. No leaks were found when the samples were tested at 450° with a helium leak detector.

Compositions of the Alloys.—After the thermal measurements one sample of each of the three alloys was analyzed at the National Bureau of Standards. After opening the container under heptane and converting the sample to the hydroxides, the following independent analyses were successively made: (a) titration with hydrochloric acid, (b) weighing the mixed chlorides, and (c) precipitation of the potassium as chloroplatinate under conditions found accurate for known similar samples. Method (a) was found relatively inaccurate under the existing conditions. But methods (b) and (c) are believed to have given highly accurate results, and the sample masses and weight compositions adopted were computed from these data alone. These values were, respectively: (1) 4.0182 g., 44.80% potassium; (2) 4.9182 g., 53.64% potassium; (3) 5.6419 g., 78.26% potassium.

The masses of samples (1) and (2) were determined by weighing just before analysis, as well as when first introduced into the containers. These check determinations disagreed by 4% for sample (1) and 1% for sample (2). The evidence strongly favors the approximate correctness of the later values for the sample masses, since the percentages of potassium, when computed using these masses and the masses of chloroplatinate, do not differ from the above values by more than 0.05%. The other possible combinations of the data show a similar correlation. A similar use of the original sample mass of sample (3) showed exact agreement with the above composition value.

Calorimetric Procedure.—The method and original apparatus were described previously in two papers.[4] The improved model of the apparatus used for the present measurements is described in detail in two more recent papers.[3,5] Briefly, the sample is heated in a furnace to a known temperature and then is dropped into an ice calorimeter that measures the heat evolved in cooling the sample to 0°. By repeating at a number of furnace temperatures, the heat capacity can be derived by the usual methods.

The calorimeter and furnace core were filled with helium, not only to minimize oxidation of the stainless steel sample containers but also to accelerate the attainment of thermal equilibrium. The time necessary for equilibration was determined by special tests.[4] The heat capacity of the sample container and the heat lost during the drop into the calorimeter were accounted for by similar experiments on empty containers of the same shape, mass and composition. The furnace temperatures were measured up to 600° by a platinum resistance thermometer whose ice point was frequently redetermined, and above 600° by a platinum–platinum-rhodium thermocouple, both calibrated at the National Bureau of Standards.

As all the containers enclosing samples were made from the same stock of stainless steel No. 347 tubing and had the same mass and shape as those used in the sodium measurements,[3] it was believed unnecessary to construct new empty containers for the present "blank" measurements. Instead, new measurements were made over the whole temperature range with the same two empty containers used previously. The results agreed closely up to 300° with those obtained five months earlier. Above 300° the more recent values were consistently about 0.2% lower than those obtained formerly. No reasonable explanation of this change has been found. The new values were used without smoothing to calculate the heat values of the three alloys. In the case of potassium, blank values were needed for interpolated temperatures in the range 0–100°. It was more convenient to use smoothed blank values, in this temperature range, calculated by plotting the smoothing function

$$\frac{q_t - q_0}{1.86t + 0.0025t^{1.73}} \qquad (1)$$

where $q_t - q_0$ represents the heat evolved between temperatures t and 0°. This function had been found in measurements on mercury[6] to vary only 1% for such stainless steel No. 347 containers over this temperature range. The smoothed values for the "blanks" were obtained by multiplying by the denominator of this function the value of the function read from the smooth curve.

Small corrections were applied to the heat measurements in order to bring the results in a given set to the basis of the same temperature, mass of container (16.8400 g.), and mass of oxide on the container surface. All weights were corrected to a vacuum basis. It was necessary at the higher temperatures to apply small corrections for the heat evolved in condensing some alkali-metal vapor inside the container, by using the following equation[7] to calculate the relative enthalpies of the liquid metals from the measured heats

$$[Q]_1^2 = [q - PV + mH + (V - mv)T\mathrm{d}P/\mathrm{d}T]_1^2 \quad (2)$$

where $[Q]_1^2$ is the heat evolved in cooling a closed container in which there is a liquid in equilibrium with its vapor from temperature 2 (the furnace temperature) to temperature 1 (0°); $[q]^2$ is the contribution to $[Q]_1^2$ made by the empty container, shields, and suspension wire; P is the vapor pressure of the liquid; V is the internal volume of the container; m is the total mass of liquid and vapor; H and v are the enthalpy and volume, respectively, of the liquid per unit mass and at pressure P; and T is the absolute temperature. The values of P and v were taken from the literature, and need not be highly accurate in the present case.

In the runs on the empty containers, the 100% potassium, and the 78% potassium alloy, the usual time of 10 or 15 min. was adequate for the attainment of equilibrium after the sample had dropped into the calorimeter. In the case of the other two alloys, this was usually far from true. With the 54% potassium alloy, 30 min. in the calorimeter was adequate for furnace temperatures of 400° or lower. For higher furnace temperatures, periods of from two to five hours were required, but at the end of such a period of time the evolution of heat from the sample ceased abruptly. The slightly inferior precision in some of the results for this composition may be due largely to the added uncertainty in evaluating the heat leak of the calorimeter over such unusually long times.

In the measurements on the 45% potassium alloy, the approach to equilibrium in the calorimeter was much slower. Though the heat evolution was always followed for many hours after the sample entered the calorimeter (in two instances for 10 and 12 hours), the rate of heat input to the calorimeter decreased greatly and approached the heat

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(4) D. C. Ginnings and R. J. Corruccini, *J. Research Natl. Bur. Standards*, **38**, 583, 593 (1947).

(5) D. C. Ginnings, T. B. Douglas and Anne F. Ball, THIS JOURNAL, **73**, 1236 (1951).

(6) T. B. Douglas, Anne F. Ball and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **46**, 334 (1951).

(7) N. S. Osborne, *Bur. Standards J. Research*, **4**, 609 (1930).

leakage from the room, but in no instance indicated that the sample had ceased to evolve heat. It was necessary therefore, in the case of this alloy, to extrapolate the heat evolution to infinite time. During the first hour the decrease of heat flow was irregular. It became so regular later, however, that a simple exponential extrapolation was made to infinite time using the readings at 150, 225 and 300 min. Each of these readings was first corrected by the heat-leak rate observed on the calorimeter just before the sample had been admitted.

The solid-liquid phase diagram of the system potassium-sodium has been determined by several workers from cooling curves.[8] This diagram gives a qualitative explanation of the different behaviors exhibited by the present samples in the ice calorimeter. At 0° pure potassium is completely crystalline and the 78% potassium alloy is completely liquid. The other two alloys, although completely liquid at 50° (the lowest furnace temperature used), undergo partial or complete crystallization on being cooled to 0°. The 54% potassium alloy deposits first a small amount of crystalline sodium, which below 7° is transformed into crystalline Na_2K, more of which then forms. It is reasonable to assume that the slower evolution of heat from this sample is due to the transformation of the crystalline sodium first formed, and that the observed sudden cessation of heat evolution coincides with the disappearance of this phase, whose transformation should be facilitated by the constant presence of a considerable amount of liquid even at 0°.

However, in cooling the liquid 45% potassium alloy considerable crystalline sodium deposits before 7° is reached, after which nearly all the sodium must be transformed into crystalline Na_2K. Since equilibrium at 0° corresponds to the complete disappearance of the liquid phase, it is reasonable to expect the later stages of equilibration to be very slow, as was observed.

These considerations suggest an explanation of the observed fact that the 54% potassium alloy showed an appreciably slow equilibration at 0° only after having been heated to as high a temperature as 500°. Sufficient distillation into the vapor space may have occurred as to impoverish appreciably the liquid with respect to potassium, with the resulting deposition of extra crystalline sodium that on further cooling had to be transformed into Na_2K.

An alternative sample of potassium was run at six temperatures, at any one of which the difference between the mean heats, as found for the two samples, did not exceed 1.1 joules per g. or 0.4%, whichever is greater. These differences seem to be largely random. Similar use of an alternative sample of the 78% potassium alloy at 300 and 800° gave results agreeing within 0.3 joule per g. (0.1 to 0.5%). No suitable alternative samples of the other two alloys were available.

For the "blanks" (empty containers) at a given temperature the deviation from the mean heat[9] was 0.03% on the average. The corresponding deviations in the case of the samples averaged about 0.06% for the 78% and 54% potassium alloys, and about 0.10% for the 100% potassium, these figures being based not on the total measured heat but only on the net heat due to the sample itself. Measurement on the 45% potassium alloy was repeated at 600° only, where the two heat values differed by 0.17% of the heat due to the sample. The latter was in each case only about half that due to the container.

Triple Point of Potassium.—The sample of potassium that had been used in the enthalpy measurements was melted in successive stages and the equilibrium temperatures were measured. The procedure followed was somewhat similar to that used for sodium.[3] Measured quantities of electrical energy were supplied to the potassium by means of a constantan heater inside a copper sheath that fitted around the sample container with an air gap of less than 0.002 inch. After each such interval of heating, the furnace temperature was adjusted to some value that was within 0.01° of that of the sample at equilibrium. The furnace temperature was maintained constant to within ±0.0005° long enough (about 20 min.) to permit the temperature difference between the sample and the furnace to become constant. This temperature difference was measured by a four-junction constantan chromel-P thermocouple, whose readings were taken entirely by deflection, the galvanometer sensitivity being determined by occasionally adjusting the furnace to a slightly different temperature and waiting for a new steady-state reading. An effort was made to eliminate or correct for the spurious electromotive forces. As the heat transfer through the air between the furnace wall and the sample reduced the temperature difference by about 1% per min. during fusion of this sample, it was necessary to apply small corrections for this heat leak.

In accordance with Raoult's law the temperature of such a sample should be a linear function of the reciprocal of the fraction that has been melted. On the basis of the most consistent points obtained, the temperatures were considerably too high before half the sample had melted. This had been observed also on several samples of sodium, and is thought to be due to an uneven distribution of the impurities in the liquid during the earlier stages of fusion. However, five equilibrium temperatures determined between 70 and 95% completion of fusion of the potassium agreed with the best linear relation to within an average of ±0.001°, though the total temperature change involved was more than 0.2°. The extrapolation to abscissa values of unity and zero indicated, respectively, that this sample of potassium had a melting point of 62.58° and that, since the pressure was small (25 mm.), the triple point of the pure element is 63.20°. This melting point depression corresponds to a liquid-soluble, solid-insoluble impurity of 0.15 atomic %, a value that is consistent with the similar total amount of impurities found in the sample by spectrochemical analysis. The melting point of potassium at one atm. pressure is calculated to be 0.02° higher than the triple point.

Enthalpy Data

The mean measured heat for each sample and its container, at each furnace temperature (International Temperature Scale of 1948[10]), is given in Tables I–IV, together with the average deviation from the mean.[9] These values have been fully corrected except for the unknown heat lost in dropping into the calorimeter, which approximately canceled out in subtracting the "blank" values of Table I to obtain the net heat due to the sample ($H_t - H_0$ or $H_t - H_{50}$). When two samples of the same composition were run at the same temperature, the over-all mean was obtained by weighting the mean for each such sample proportionately to the number of measurements on it at that temperature and inversely proportionately to the average deviation from the mean for that sample. The calculated values referred to in the last column of Tables II–IV were obtained from the empirical equations given later.

TABLE I

EMPTY CONTAINERS

Furnace temp. t, °C.	Measured heat[9] (mean), $[q]_0^t$ abs. joules[a]	No. of runs	Furnace temp. t, °C.	Measured heat[9] (mean), $[q]_0^t$ abs. joules[a]	No. of runs
50.00	400.63 ± 0.64	3	400.00	3493.22 ± 0.75	3
100.00	811.82 ± 1.60	3	500.00	4440.67 ± 1.50	8
150.00	1240.57 ± 1.18	3	600.00	5409.22 ± 1.75	5
200.00	1675.66 ± 0.77	3	699.6	6403.96 ± 0.84	3
300.00	2570.22 ± 1.20	6	796.9	7399.77 ± 1.80	7

[a] 4.1840 absolute joules = 1 defined cal.

Derived Properties

Relative Enthalpy; Heat of Fusion of Potassium.—The observed enthalpy values at the "saturation" (vapor) pressures are represented, in absolute joules per g. at t, °C., by the following empirical equations. Those for sodium previously given[3] are included for reference and to complete the series. In equation (9) the exponential term originally given has been replaced by the algebraic term

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(8) "International Critical Tables," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1927, p. 436.

(9) In this paper each average deviation from the mean has been adjusted to the basis of an infinite number of observations by multiplying by the factor $\sqrt{n/(n-1)}$, where n is the number of observations actually made.

(10) H. F. Stimson, *J. Research Natl. Bur. Standards*, **42**, 209 (1949).

TABLE II

Furnace temp., t, °C.	Measured heat[9] (mean), $[Q]_0^t$ abs. joules	No. of runs	Relative enthalpy ($H_t - H_0$) Mean observed abs. joules g.$^{-1}$	Relative enthalpy ($H_t - H_0$) Calcd. – observed abs. joules g.$^{-1}$
	100% Potassium[a]			
25.456	288.04 ± 3.36	5	19.451	−0.694
30.60	345.28 ± 0.57[b]	3	22.769	− .058
	344.73 ± 1.83	3		
38.00	429.12 ± 0.32	3	28.439	+ .056
45.00	511.45 ± 0.82	3	34.154	− .083
52.00	593.39 ± 0.46	3	39.715	+ .034
59.00	682.37 ± 0.96[b]	3	45.430	+ .099
	674.94 ± 1.07	6		
65.00	1018.65 ± 0.70[b]	3	110.186	+ .001
	1014.26 ± 0.76	3		
100.00	1440.74 ± 2.00[b]	5	138.595	+ .179
	1430.73 ± 0.49	3		
150.00	2036.04 ± 2.21	4	179.084	− .004
200.00	2648.61 ± 1.52	3	219.045	− .215
300.00	3889.14 ± 1.22	3	296.934	+ .043
400.00	5153.57 ± 0.66	3	373.807	+ .038
500.00	6440.37 ± 1.32	3	450.144	− .080
	6465.66 ± 0.34[b]	3		
600.00	7745.63 ± 0.61	3	526.046	+ .218
699.6	9081.43 ± 0.80	3	602.906	− .141
796.9	10408.72 ± 2.68	4	678.854	− .172
	10454.30 ± 0.94[b]	3		
	78.26% Potassium–21.74% sodium[c]			
50.00	677.00 ± 1.15	4	48.986	−0.020
100.00	1359.16 ± 1.01	3	96.730	− .138
150.00	2047.73 ± 1.03	3	143.059	+ .104
200.00	2741.18 ± 1.48	3	188.866	+ .043
300.00	4143.01 ± 0.84	3	278.571	+ .057
	3642.30 ± 0.75[d]	3		
400.00	5563.42 ± 1.88	3	366.916	− .048
500.00	7004.99 ± 1.54	4	454.495	− .070
600.00	8466.44 ± 2.55	4	541.870	+ .035
699.6	9954.50 ± 1.25	3	629.353	+ .109
796.9	11437.19 ± 1.19	3	715.970	− .134
	10156.41 ± 0.55[d]	3		

[a] Solid below 63.2°. [b] On alternate container, containing 4.4981 g. of potassium. (The other container had the same mass but contained 4.4418 g. of potassium.) [c] Sample entirely liquid at 0° and above. [d] One alternate container, containing 3.8509 g. of sample. (The other container had the same mass but contained 5.6419 g. of sample.)

TABLE III

53.64% POTASSIUM–46.36% SODIUM[a]

Furnace temp., t, °C.	Measured heat[9] (mean), $[Q]_0^t$ abs. joules	No. of runs	Relative enthalpy ($H_t - H_{50}$) Mean observed abs. joules g.$^{-1}$	Relative enthalpy ($H_t - H_{50}$) Calcd. – observed abs. joules g.$^{-1}$
50.00	1075.73 ± 1.43	4	....	....
100.00	1759.24 ± 1.74	3	55.02	−0.01
150.00	2455.83 ± 0.87	3	109.83	− .88
200.00	3145.98 ± 3.40	4	161.38	+ .56
300.00	4554.59 ± 1.13	4	266.19	− .64
400.00	5971.60 ± 1.11	3	366.64	+ .11
500.00	7405.74 ± 0.15	2	465.60	+ .87
600.00	8867.05 ± 2.22	2	565.80	− .16
699.6	10350.82 ± 0.27	2	665.30	− .52
796.9	11825.66 ± 3.08	2	762.79	+ .08

[a] Sample entirely liquid at 50° and above, but partly solid at 0°. Sample mass, 4.9182 g.

TABLE IV

44.80% POTASSIUM–55.20% SODIUM[a]

Furnace temp., t, °C.	Measured heat, $[Q]_0^t$, abs. joules 0 to 150 min.	Measured heat 150 to 300 min.	Measured heat 300 min. to ∞	Measured heat Total	Enthalpy ($H_t - H_{50}$) Observed abs. joules g.$^{-1}$	Enthalpy ($H_t - H_{50}$) Calcd. – obsd. abs. joules g.$^{-1}$
50.00	1033.5	14.7	10.3	1058.5	....	....
100.00	1664.0	16.4	18.2	1698.6	56.53	+0.23
200.00	2983.3	14.1	18.2	3015.6	169.70	−1.96
300.00	4314.2	15.6	10.5	4340.3	276.77	−1.07
400.00	5643.7	16.3	18.1	5678.1	379.99	+1.64
500.00	7017.8	15.6	15.3	7048.7	485.30	+0.92
600.00	8427.3	14.9	8.4	8450.6	593.79	−3.56
	8423.7	17.0	15.0	8455.7		
682.3	9573.4	16.0	9.1	9598.5	674.67	+1.25
796.9	11198.7	16.0	30.2	11244.9	793.12	+3.12

[a] Sample entirely liquid at 50° and above, but entirely solid (two phases) at 0°. Sample mass, 4.0182 g.

$+1.46(10^{-10})\ t^3$, giving an equation that represents the data as well as the original equation.

SOLID POTASSIUM: $H_t(\text{solid}) - H_0(\text{solid}) = 0.71040\ t + 1.0385(10^{-3})t^2$ (0 to 63.2°) (3)

LIQUID POTASSIUM: $H_t(\text{liquid}) - H_0(\text{solid}) = 56.179 + 0.840741t - 1.58440(10^{-4})t^2 + 1.04993(10^{-7})t^3$ (63.2 to 800°) (4)

LIQUID 78.26% K, 21.74% NA: $H_t(\text{liquid}) - H_0(\text{liquid}) = 0.93860\ t - 1.09621(10^{-4})t^2 + 7.0555\ (10^{-8})t^3 + 0.05636\ t\ e^{-0.00405494t}$ (0 to 800°) (5)

LIQUID 53.64% K, 46.36% NA: $H_t(\text{liquid}) - H_0(\text{liquid}) = 1.13625\ t - 2.5899(10^{-4})\ t^2 + 1.5422\ (10^{-7})\ t^3$ (50 to 800°) (6)

LIQUID 44.80% K, 55.20% NA: $H_t(\text{liquid}) - H_0(\text{liquid}) = 1.16587\ t - 2.19091(10^{-4})\ t^2 + 1.26579\ (10^{-7})\ t^3$ (50 to 800°) (7)

SOLID SODIUM: $H_t(\text{solid}) - H_0(\text{solid}) = 1.19926\ t + 3.247(10^{-4})\ t^2 + 3.510(10^{-6})t^3$ (0 to 97.8°) (8)

LIQUID SODIUM: $H_t(\text{liquid}) - H_0(\text{solid}) = 98.973 + 1.436744\ t - 2.90244(10^{-4})t^2 + 1.54243(10^{-7})t^3$ (97.8 to 900°) (9)

Equations (3) and (4) give a value of 59.67 absolute joules per g. for the heat of fusion of potassium at 63.2°, the triple point as found by the authors.

Heat Capacity.—The heat capacity C_s along the saturation path was obtained from the relative enthalpy by the relation

$$C_s = \frac{dH}{dt} - v\frac{dP}{dt} \qquad (10)$$

where v is the specific volume of the liquid and P is the vapor pressure. Since this correction term, $v\ dP/dt$, is relatively small (not more than a few tenths of 1%), even at the highest temperatures, it was possible to express it approximately as a function of t^2 and to combine it with the t^2 term obtained by differentiating the corresponding equation for H.[11] The relative smallness of the correction term, as well as the degree of precision of the heat capacity data for these materials, does not seem to justify the use of a more refined expression than a quadratic term. Accordingly, equations for the

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(11) In the paper describing the work on sodium[8], the treatment of this correction term is somewhat different. It was approximated by the assumption that v is essentially constant with temperature. A term Pv was used to account for the difference between enthalpy H and heat evolution Q. Since the sample container was almost full at the highest temperatures, the term was written as PV/m, where V is the volume of the sample container and m is the mass of sample.

heat capacities have been obtained by differentiating the equations for enthalpies and then subtracting the following terms (abs. joules g.$^{-1}$): for liquid potassium, 6.27 $(10^{-10})t^2$; for the 78% potassium alloy, 7.53 $(10^{-10})t^2$; and for liquid sodium, 4.38 $(10^{-10})t^2$. No corresponding terms have been subtracted in the other cases, since their maximum magnitudes would lie well within the precision of the original thermal data.

The heat capacity equations so obtained are as follows, the units being absolute joules per gram-° C. at t°.

SOLID POTASSIUM: $C_s = 0.71040 + 2.0770(10^{-3})t$ (0 to 63.2°) (11)

LIQUID POTASSIUM: $C_s = 0.84074 - 3.1688(10^{-4})t + 3.1435(10^{-7})t^2$ (63.2 to 800°) (12)

LIQUID 78.26% K, 21.74% NA: $C_s = 0.93860 - 2.1924(10^{-4})\ t + 2.1091(10^{-7})\ t^2 + 0.05636\ (1 - 0.0040549t)e^{-0.0040549t}$ (0 to 800°) (13)

LIQUID 53.64% K, 46.36% NA: $C_s = 1.13625 - 5.1798(10^{-4})\ t + 4.6266(10^{-7})\ t^2$ (50 to 800°) (14)

LIQUID 44.80% K, 55.20% NA: $C_s = 1.16587 - 4.3818(10^{-4})\ t + 3.7974(10^{-7})\ t^2$ (50 to 800°) (15)

SOLID SODIUM: $C_s = 1.19926 + 6.494(10^{-4})\ t + 1.0531(10^{-5})t^2$ (0 to 97.8°) (16)

LIQUID SODIUM: $C_s = 1.43674 - 5.8049(10^{-4})t + 4.6229(10^{-7})t^2$ (97.8 to 900°) (17)

Values of heat capacity calculated from these equations for rounded temperatures are given in Table V.

TABLE V

Temp., °C.	Heat capacity (C_s) (abs. joules g.$^{-1}$ °C.$^{-1}$)				
	Potassium	78.26% K	53.64% K	44.80% K	Sodium
0	0.7104[a]	0.9950			1.1991[a]
25	.7623[a]	.9790			1.2221[a]
50	.8142[a]	.9649	1.1115	1.1449	1.2555[a]
75	.8187	.9523	1.1000	1.1352	1.3071[a]
100	.8122	.9411	1.0891	1.1259	1.3832
200	.7899	.9079	1.0512	1.0934	1.3393
300	.7740	.8882	1.0225	1.0686	1.3042
400	.7642	.8777	1.0031	1.0514	1.2786
500	.7609	.8741	0.9929	1.0417	1.2619
600	.7638	.8759	0.9920	1.0397	1.2548
700	.7729	.8824	1.0004	1.0452	1.2569
800	.7884	.8933	1.0180	1.0584	1.2682
900					1.2887

[a] For the solid. The other values of the table are for the liquid state.

Relative Entropy.—From the heat capacity equations may be obtained the entropy (also at saturation pressure) in excess of that at 0°C. The equations for potassium and sodium follow, the units being abs. joules g.$^{-1}$ °K.$^{-1}$ and T representing °K. (with 0°C. = 273.16°K.).

SOLID POTASSIUM: $S_{\mathrm{T}}(\text{solid}) - S_{273.16°K.}(\text{solid}) = 0.32938 \log_{10}T + 2.0770(10^{-3})T - 1.36986$ (0 to 63.2°) (18)

LIQUID POTASSIUM: $S_{\mathrm{T}}(\text{liquid}) - S_{273.16°K.}(\text{solid}) = 2.18919 \log_{10}T - 4.8862(10^{-4})T + 1.5718(10^{-7})T^2 - 5.04665$ (63.2 to 800°) (19)

SOLID SODIUM: $S_{\mathrm{T}}(\text{solid}) - S_{273.16°K.}(\text{solid}) = 4.16241 \times \log_{10}T - 5.1036(10^{-3})T + 5.2656(10^{-6})T^2 - 9.14016$ (0 to 97.8°) (20)

LIQUID SODIUM: $S_{\mathrm{T}}(\text{liquid}) - S_{273.16°K.}(\text{solid}) = 3.75276 \log_{10}T - 8.3303(10^{-4})T + 2.3112(10^{-7})T^2 - 8.67398$ (97.8 to 900°) (21)

Reliability.—Values of the precision obtained are given in Tables I–IV. As for the likely systematic errors, there can be applied to the present measurements without change the same estimates given in the paper on sodium[3] with regard to the limits of error in temperature measurement, in accounting for the heat lost during the drop into the calorimeter, in the extent of dissolving of the container, and in the use of measurements on water to check the over-all accuracy. These particular errors are believed to aggregate less than 0.1% of the enthalpy. Nor should the impurities in the samples contribute major error. However, other sources of error are more serious. The measurements of enthalpy on alternate samples of 100% potassium disagreed at some temperatures by several tenths of 1% for the solid and about 0.1% on the average for the liquid. As noted earlier, some of the present heat values of the empty containers differed inexplicably by as much as 0.2% from those obtained previously. The enthalpy values of the liquid 45% potassium alloy are rendered further uncertain by the necessity of extrapolating to infinite time and by the lack of knowledge of whether the final state being approached by the sample in the calorimeter varied somewhat systematically with furnace temperature.

After statistically combining estimates of these errors and other less significant ones, the authors were led to believe that the errors in the enthalpy values given by the equations are not greater than the following amounts (except in the case of the liquids below 200°, where the enthalpy is relatively small): for solid potassium, 1 to 2%; for liquid potassium, 0.3%; for the 78% potassium alloy, 0.3%; for the 54% potassium alloy, 0.5%; and for the 45% potassium alloy, 1%. The following uncertainties have been assigned to the respective heat capacity values calculated from the equations (except below 100° and above 700°): 2%, 0.4%, 0.4%, 0.5 to 1%, and 1 to 2%. These uncertainties of heat capacity values were arrived at without consideration of the deviations from the additively calculated values shown in Fig. 1, where it is seen that the deviations from additivity of the most precisely measured alloy (78% potassium) are small. If this is also true of the other two alloys, then the uncertainties assigned to their heat capacities are probably not underestimated.

The triple point found for pure potassium, 63.20°, is considered to have a probable uncertainty of 0.1°, which is largely to be attributed to the 0.6° extrapolation necessary because of the impurity in the sample. The earlier paper on sodium[3] had reported measurements that led to a value of the triple point of pure sodium of 97.80 ± 0.03°. Since in the present melting apparatus a very stable platinum resistance thermometer replaced the relatively unstable copper resistance thermometer previously used, this constant was redetermined on four different samples of sodium that yielded a value of 97.82 ± 0.02°. This temperature, which agrees with the earlier value within the tolerance assigned to the latter, has as its principal source of uncertainty the dependability of the differential thermocouple readings. The experimental set-up

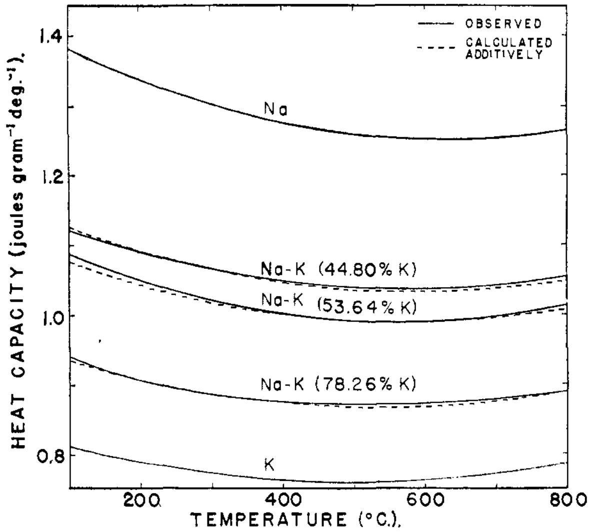

Fig. 1.—Heat capacity of the liquid system potassium-sodium.

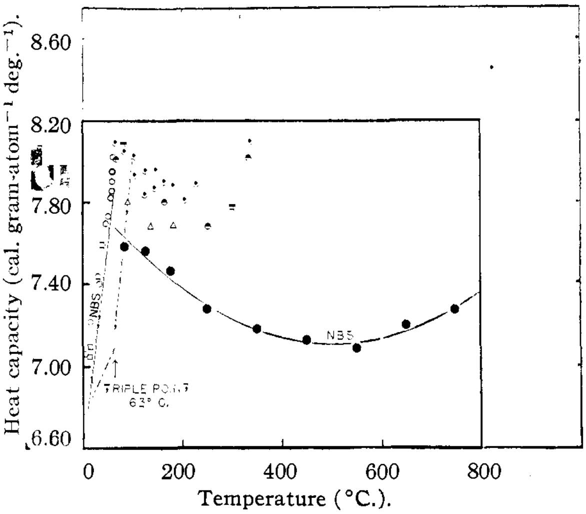

Fig. 2.—Heat capacity of potassium as observed by various investigators: —, NBS (smoothed) (1950); ●, NBS (experimental); — - — - —, Rengade (1913); ⊖, Carpenter and Steward (liquid) (1939); ○, Carpenter and Steward (solid); △, Dixon and Rodebush (1927); □, Eastman and Rodebush (1918).

is estimated to have yielded such accuracy, despite the large coefficient of heat leakage, owing to the very high thermal conductivity of the metallic samples and their relatively small temperature changes during the significant stages of fusion.

In accordance with the uncertainties estimated above for the enthalpy of solid and liquid potassium in the neighborhood of the triple point, the value given for the heat of fusion of potassium is assigned an uncertainty of ±2%. It is believed that very little error was contributed by appreciable "premelting" (caused by impurities) at the highest temperature at which the enthalpy of the solid was measured, 59°. For, as shown in Table II, the mean observed value of enthalpy at this temperature is not higher than that indicated by the linear trend, with temperature, of the values for solid potassium at lower temperatures.

Discussion

Apparently no one has reported measurements of the heat capacities of potassium–sodium alloys. Such measurements have been reported for potassium, however, and these are shown in Fig. 2 for comparison with those of the present investigation. The solid curves labeled "NBS" represent the present results as calculated by equations (11) and (12). Each experimental point accompanying the "NBS" curve for the liquid was computed by dividing by the temperature difference the difference in two successive unsmoothed ("Observed") enthalpies in Table II, and applying the very small correction for curvature. Rengade[12] used an ice calorimeter. His values, especially for the liquid, were apparently subject to a large systematic error. Eastman and Rodebush[13] (most of whose measurements were made below 0°) used an adiabatic method and claimed an accuracy of better than 1%. Dixon and Rodebush[14] made a few measurements on the liquid by a method measuring the adiabatic temperature–pressure coefficient. Carpenter and Steward[15] used a Nernst-type nickel calorimeter. Their measurements on potassium extended to higher temperatures than any reported prior to the present investigation. Their heat capacity values are several per cent. higher than those of the authors, and obviously their precision was considerably inferior.

A number of observers have reported values for the melting point and heat of fusion of potassium. These are listed in Table VI.

TABLE VI

M.p., °C.	Heat of fusion (abs. joules g.⁻¹)	Source
63.2	59.7	This investigation
63.7	..	Walters and Miller[16]
63.35	60.8	Carpenter and Steward[15]
63.65	..	Edmondson and Egerton[17]
62.4	..	Geurtler and Pirani[18]
...	53.6	Bridgman[19]
63.50	61.4	Rengade[12]
62.5	..	van Bleiswijk[20]
...	56.7	Bernini[21]
62.5	..	Kurnakow and Puschin[22]
...	65.3	Joannis[23]

The "observed" heat capacity curves of Fig. 1, calculated from the empirical equations, show close agreement with the dotted curves, calculated from the equations for the pure liquid elements with the assumption of additivity. The smallness of the

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[12] E. Rengade, *Compt. rend.*, **156**, 1897 (1913).

[13] E. D. Eastman and W. H. Rodebush, THIS JOURNAL, **40**, 489 (1918).

[14] A. L. Dixon and W. H. Rodebush, *ibid.*, **49**, 1170 (1927).

[15] L. G. Carpenter and C. J. Steward, *Phil. Mag.*, **27**, 551 (1939).

[16] S. L. Walters and R. R. Miller, *Ind. Eng. Chem., Anal. Ed.*, **18**, 468 (1946).

[17] W. Edmondson and A. Egerton, *Proc. Royal Soc. (London)*, **A113**, 520 (1927).

[18] Geurtler and Pirani, *Z. Metallkunde*, **11**, 1 (1919).

[19] P. W. Bridgman, *Phys. Rev.*, **3**, 153 (1914).

[20] G. L. C. M. van Rossen Hoogendijk van Bleiswijk, *Z. anorg. Chem.*, **74**, 152 (1912).

[21] A. Bernini, *Physik. Z.*, **7**, 168 (1906).

[22] N. S. Kurnakow and N. A. Puschin, *Z. anorg. Chem.*, **30**, 109 (1902).

[23] A. Joannis, *Ann. Chem. Phys.*, [7] **12**, 358 (1887).

deviations from additivity explains the regularly rising temperature of minimum heat capacity as the proportion of potassium to sodium decreases, these observed temperatures being, respectively, 504, 514, 560, 577 and 628° for 100, 78, 54, 45 and 0% potassium. It is noteworthy that these temperatures (in °K.) are 75 and 78% of the normal b.p.'s in the cases of pure potassium and sodium, respectively. This last correspondence is perhaps not particularly unexpected for two elements that are so similar in other properties.

Though these deviations of the heat capacities of the alloys from additivity are almost within the assigned uncertainties, there is a strong indication that they tend to be positive. It is worth mentioning that whereas for pure liquid potassium and sodium there were found cubic equations ((4) and (9)) that represent the observed enthalpy without apparent trend over the investigated temperature range, this seemed not to be the case for the one alloy (78% potassium) measured with maximum precision. The introduction of an exponential term into the enthalpy equation for this alloy (equation (5)) eliminated the trend otherwise present. This provides some evidence that the true heat-capacity, temperature curve of this alloy possesses a greater curvature at the lower temperatures and a smaller curvature at the higher temperatures than the corresponding additively calculated curve. This may have some theoretical significance.

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3,4-Dithiahexane: Heat Capacity, Heats of Fusion and Vaporization, Vapor Pressure, Entropy, and Thermodynamic Functions[1]

BY D. W. SCOTT, H. L. FINKE, J. P. MCCULLOUGH, M. E. GROSS, R. E. PENNINGTON AND GUY WADDINGTON

RECEIVED DECEMBER 7, 1951

The following thermodynamic properties of 3,4-dithiahexane were determined experimentally: heat capacity of the solid and liquid between 12 and 300°K., triple point (171.64°K.), heat of fusion (2248 cal. mole^{-1}), vapor pressure ($\log_{10} p = 6.97507 - 1485.970/(t + 208.958)$), heat of vaporization (9780 and 9380 cal. mole^{-1} at 373.73 and 400.04°K., respectively), entropy of the vapor (S^0 = 107.31 and 109.96 cal. deg.$^{-1}$ mole^{-1} at 373.73 and 400.04°*K*., respectively), and heat capacity of the vapor (C_p^0 = 41.41 and 42.71 cal. deg.$^{-1}$ mole^{-1} at 408.20 and 428.25°K., respectively). The functions $-(F^0 - H_0^0)/T$, $H^0 - H_0^0$, S^0, and C_p^0 were calculated from spectroscopic and molecular-structure data for selected temperatures up to 1000°K. In these calculations, a two-constant potential function for internal rotation of the ethyl groups was selected to fit the calorimetric values of the heat capacity and entropy of the vapor. Interpretation of the spectroscopic data for 3,4-dithiahexane led to the conclusion that the stable form of the molecule has both ethyl groups in the *trans*-configuration.

The investigation of the thermodynamic properties of organic sulfur compounds which is in progress in this Laboratory consists of detailed experimental and computational studies of selected members of homologous series which may be present in petroleum or be produced in refining processes. A previous paper[2] presented the results of a study of the first member of the symmetrical alkane disulfide series, 2,3-dithiabutane (dimethyl disulfide). This paper presents the results of a similar but somewhat more comprehensive study of the next higher homolog of the series, 3,4-dithiahexane (diethyl disulfide).

Experimental values were obtained for the entropy and heat capacity of the compound in the vapor state. Thermodynamic functions were then computed from spectroscopic and molecular structure data, using the experimental values of the entropy and heat capacity to evaluate certain necessary structural parameters. The results of previous studies in this Laboratory of simpler, structurally related compounds, particularly 2,3-dithiabutane and ethanethiol, were utilized in interpreting the spectra of the relatively complex 3,4-dithiahexane molecule and in treating its several internal rotations.

Experimental

The Material.—The 3,4-dithiahexane used for the experimental measurements consisted of two samples, which were prepared and purified at the Laramie Station of the Bureau of Mines as part of A.P.I. Research Project 48A. One of these samples was used for low temperature studies and vapor pressure measurements. Its purity was determined during the course of the low temperature studies by measuring the melting point as a function of the fraction melted. The value of the purity so obtained was 99.92 mole per cent. The other sample was used for heat of vaporization and vapor heat capacity measurements. The purity of this second sample, determined at the Laramie Station by the time–temperature freezing point method, was reported to be 99.91 mole per cent. Both samples, when they were not being used for measurements, were stored in the dark as a precaution against photochemical decomposition.

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(1) This investigation was performed as part of the work of American Petroleum Institute Research Project 48A on "The Production, Isolation, and Purification of Sulfur Compounds and Measurement of their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo.

(2) D. W. Scott, H. L. Finke, M. E. Gross, G. B. Guthrie and H. M. Huffman, THIS JOURNAL, **72**, 2424 (1950).