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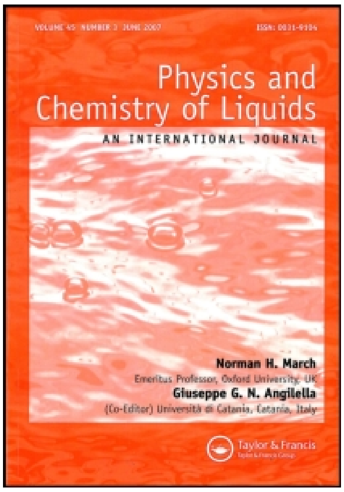

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P. W. Kendall[ab]
[a] Metallurgy Division, Atomic Energy Research Establishment, Harwell [b] Brookhaven National Laboratory, Upton, New York, U.S.A.

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The Absolute Thermoelectric Powers of the Liquid Alkali Metals†

P. W. KENDALL

Metallurgy Division, Atomic Energy Research Establishment,
Harwell, Berkshire,
England
Brookhaven National Laboratory, Upton, New York,
U.S.A.

Abstract—Data are presented on the absolute thermoelectric powers of the alkali metals, including the changes at the melting points, and a short discussion is given on the extent to which experiment and theory are now in agreement.

1. Introduction

Interest in the thermoelectric powers of liquid metals has in recent years been stimulated by the development of a theory which is capable of providing results that can be compared with experiment. This theory, due to Ziman[1] is based upon a nearly-free-electron model that might be expected to apply particularly well to the alkali metals.

Although the thermoelectric powers of the liquid alkali metals had all been measured prior to the present programme, much of the work was old and the agreement between different workers for a particular metal was not at all good; the published values for liquid Na, K, Rb, and Cs spread something like ±20% about their mean values, and for liquid lithium only one value could be found in the literature, and that dated from 1924. It was therefore thought worthwhile to make further thermoelectric power measurements on high purity samples of the alkali metals in order to compare them with the recent results by Bradley[2] and Bonilla *et al.*[3] for liquid Na, K, Rb, and Cs, and to provide a new value for liquid lithium. An additional aim of the present work was to establish accurately the changes in thermoelectric power on melting.

The experimental details of the programme will be presented in Sections 2 and 3, and a comparison between the present measurements and Ziman's theory will be made in Section 4.

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† The experimental work was performed in the Metallurgy Division of Brookhaven National Laboratory under the auspices of the U.S. Atomic Energy Commission.

2. Apparatus

One of the cells used in the present work is shown in Fig. 1. The alkali metal was put into the cell in a sealed glass ampoule which was broken with the steel rod after the cell had been evacuated. The metal was then melted and forced up into the Lucalox tube using an over-pressure of purified helium.

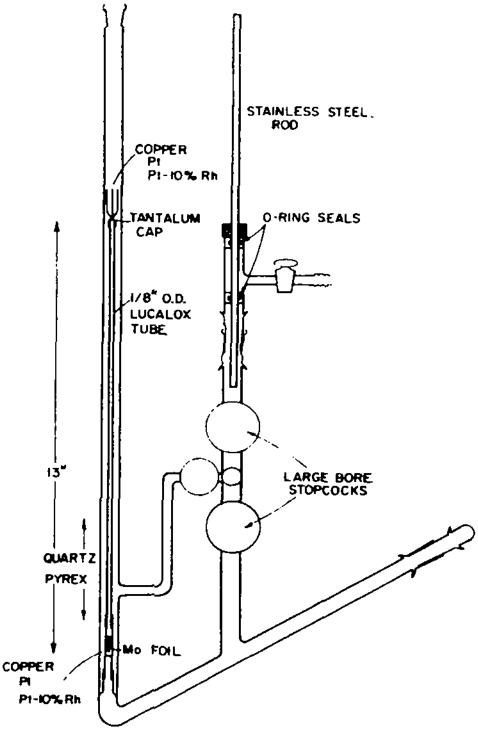

Figure 1. The "Lucalox" cell used for measurements on sodium and rubidium. The cell was designed for use with alloys and the arrangement at the right allows successive additions of solute to be made to the initial charge.

The Lucalox tube was closed at the top with a shrink-fit tantalum cap to which a Pt/Pt-Rh thermocouple and a spectrographically pure copper counter-electrode had been brazed; this formed the "hot" junction of the cell. The "cold" junction consisted of a similar arrangement of wires brazed to a piece of very thin (.002") molybdenum foil that was held with epoxy resin over a hole in the wall of the Pyrex tube just below the Lucalox.

A cylindrical furnace, wound in two sections, slipped over the measuring limb of the cell and during an experiment the temperature at the upper junction with the alkali metal was varied while the lower junction was immersed in a constant temperature oil bath. The thermal e.m.f.'s were measured on a Leeds and Northrup Type K-3 potentiometer and the Pt/Pt-10% Rh thermocouples were calibrated by comparison with an N.B.S. calibrated thermocouple; Pt/Pt-10% Rh thermocouple Test #183728.

The e.m.f. versus temperature data thus obtained were fed into a computer, which made a least squares fit with a fourth order polynomial and then printed out the thermoelectric power $\frac{dE}{dT}$ at each temperature. The thermoelectric power of two metals A and B can be written as

$$\frac{dE_{AB}}{dT} = S_B - S_A \qquad (1)$$

where S_B is the absolute thermoelectric power of metal B *etc.*, so to obtain the absolute thermoelectric power of the specimen one has to know the absolute thermoelectric power of the counter-electrode.

In the present experiment, as a check on the apparatus, measurements were made against both platinum and copper. The absolute thermoelectric power of platinum as a function of temperature was obtained by drawing a smooth curve through the values published by Cusack and Kendall[4], and the absolute thermoelectric power of copper was calculated from the linear equation used by Cusack, Kendall and Marwaha.[5]

3. Experimental Results

Sodium

Fig. 2 shows the results obtained for high purity sodium using the "Lucalox" cell described. The sodium was Du Pont reactor grade material that had been further purified (hot trapped) at B.N.L. Analysis showed that only Al, Ca, K and Si were present in concentrations of greater than 10 p.p.m.; Al 20–300, Ca 20–40, K 10–20 and Si ~75 p.p.m.

The experimental run started at 197°C, went up to 536°C, returned to confirm the initial values, and then continued on through the melting point and down to room temperature. The results are compared with some of the other values in the literature and the picture for liquid sodium is believed to be complete back to 1911, but to avoid confusion only very recent values for solid sodium have been plotted.

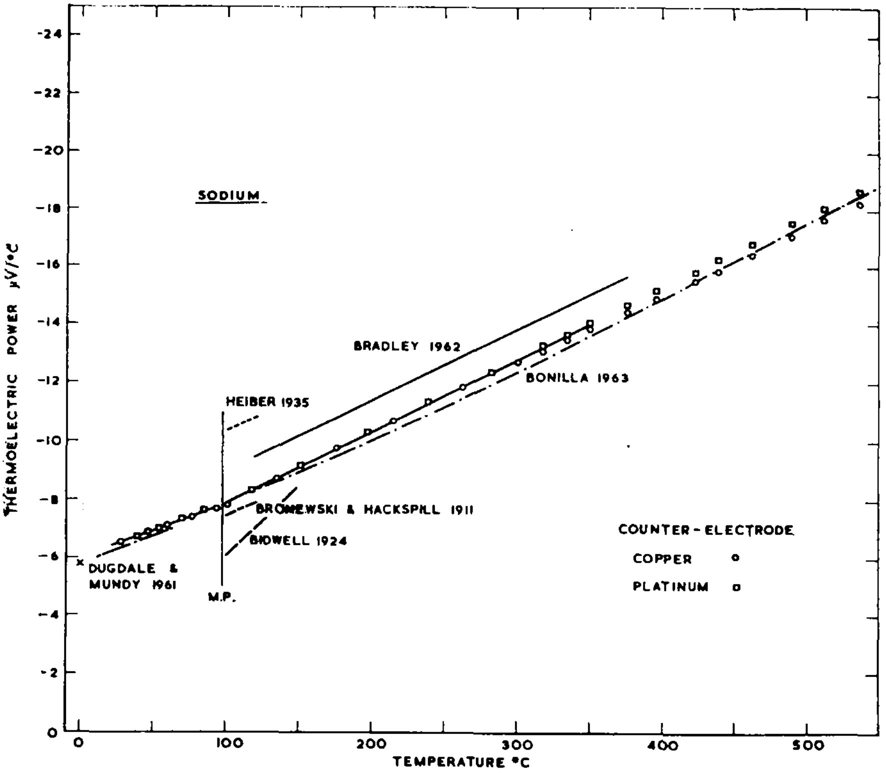

Figure 2. The thermoelectric power of sodium as a function of temperature.

Bonilla *et al.*[3] tabulated thermoelectric potentials with respect to platinum at 25°C intervals from 0°C up to at least 750°C. For the solid metals the thermoelectric power has been obtained using the ΔE and ΔT of successive readings, but for the liquids the data have been put through the same computer programme as the present results.

As with Figs. 3–6, where the present results against Cu and Pt are in close agreement they are shown alternately; elsewhere both results are shown.

Figure 2 shows that the early results for liquid sodium were limited in temperature range and somewhat scattered, whereas the recent measurements cover a wide temperature range and are in reasonably good agreement, particularly with regard to their temperature dependence. Also, the present results clearly show that there is no appreciable change in the absolute thermoelectric power of sodium on passing through the melting point. Bonilla's results are consistent with this, as indeed are the results of the earlier workers except for Bidwell[6] who found a change of ~2.5 μV/°C.

Potassium

A plot of the results obtained from one of the runs on solid and liquid potassium is shown in Fig. 3. The potassium was obtained from Mine Safety Appliances and their analysis showed no impurity exceeding 25 p.p.m.

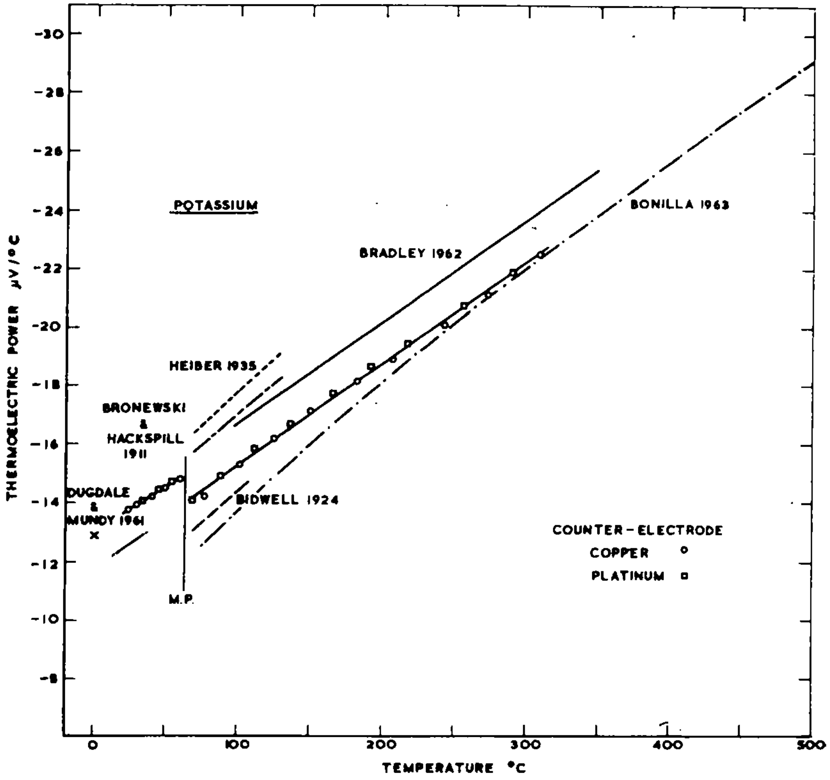

Figure 3. The thermoelectric power of potassium as a function of temperature.

The measurements do not cover such a wide temperature range as those on sodium as an earlier quartz cell was used to contain the potassium. This cell was of a similar design to that shown in Fig. 1, but the hot and cold junctions were both made on molybdenum foil that had been fused directly into the wall of the measuring limb.

The first measurements were made from the melting point up to 310°C, with the "cold" junction at 68°C. Two runs were then made through the melting point, down and then up, with the cold junction near room temperature, to establish the change on melting and to confirm the initial results for the low part of the liquid range.

Figure 3 shows that the agreement between recent measurements as to the temperature dependence of the absolute thermoelectric power of potassium is not as good as it was for sodium; Bonilla's values are seen to diverge from the line drawn through the present results as one goes from 300°C down towards the melting point, whereas the present results again fall on a line parallel to the one obtained by Bradley.[2] Also, the agreement on the change at the melting point is not as close as it was for sodium; the present value for the change on melting is $+1\ \mu$V/°C, whereas Bonilla's value is approximately $+2\ \mu$V/°C. Bronewski and Hackspill[7], Heiber[8], and Bidwell[6] found changes of 0, +1.5, and 2.0 μV/°C respectively.

Rubidium

Figure 4 shows the results obtained from solid and liquid rubidium. The rubidium was high purity material obtained from Mine Safety Appliances and the measurements were carried out using the cell shown in Fig. 1. First of all two runs were made through the melting point, with the cold junction at room temperature. Then a final run was made through the melting point and up to 350°C, with the cold junction at 43°C.

The three recent measurements on liquid rubidium are seen to be in good agreement; the temperature dependence will later be compared with some theoretical values obtained from Ziman's theory.

The present work gave just one point for solid rubidium as measurements were made over a temperature range of only 15°C in the solid state. However, the three runs through the melting point were sufficient to establish the change on melting, and the average of the six values was $+3.8 \pm 0.4\ \mu$V/°C. As Bonilla's value for solid rubidium is well

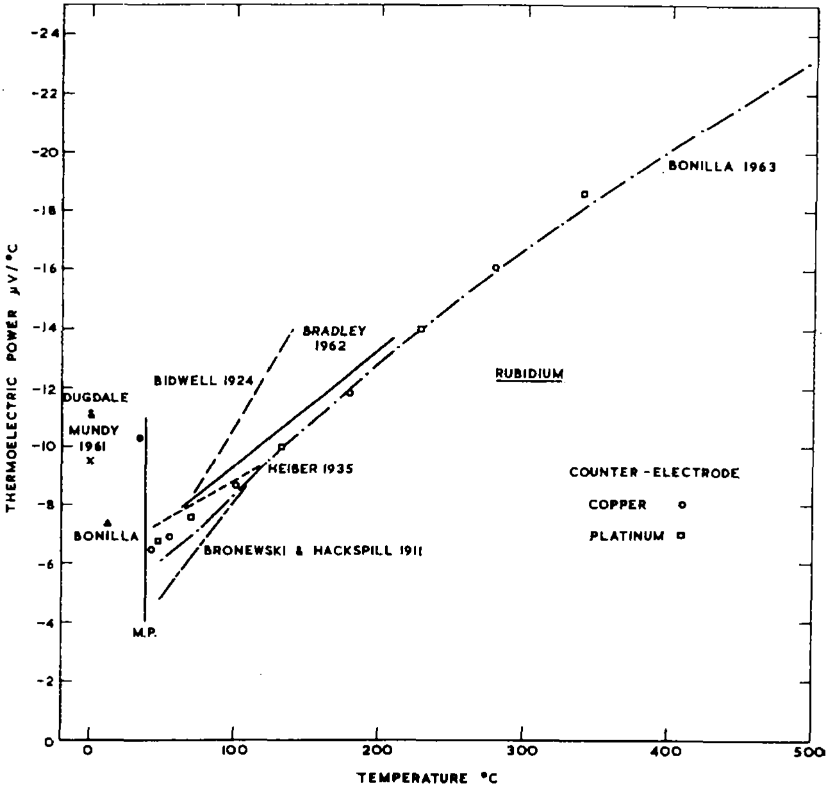

Figure 4. The thermoelectric power of rubidium as a function of temperature.

below the present value his measurements show only a small change at the melting point. Heiber, Bidwell, and Bronewski and Hackspill found changes on melting of +4.5, +5.0 and +7.0 μV/°C respectively.

Cesium

The cesium, which was obtained from Mine Safety Appliances, was contained in the quartz cell previously used for potassium and measurements were made up to 160°C.

The first run was made from 40°C upwards, with the cold junction at 36°C, and then a second run was made to confirm the initial results for the region immediately above the melting point.

In order to obtain results for solid cesium, the upper junction was maintained at room temperature while the lower junction was immersed

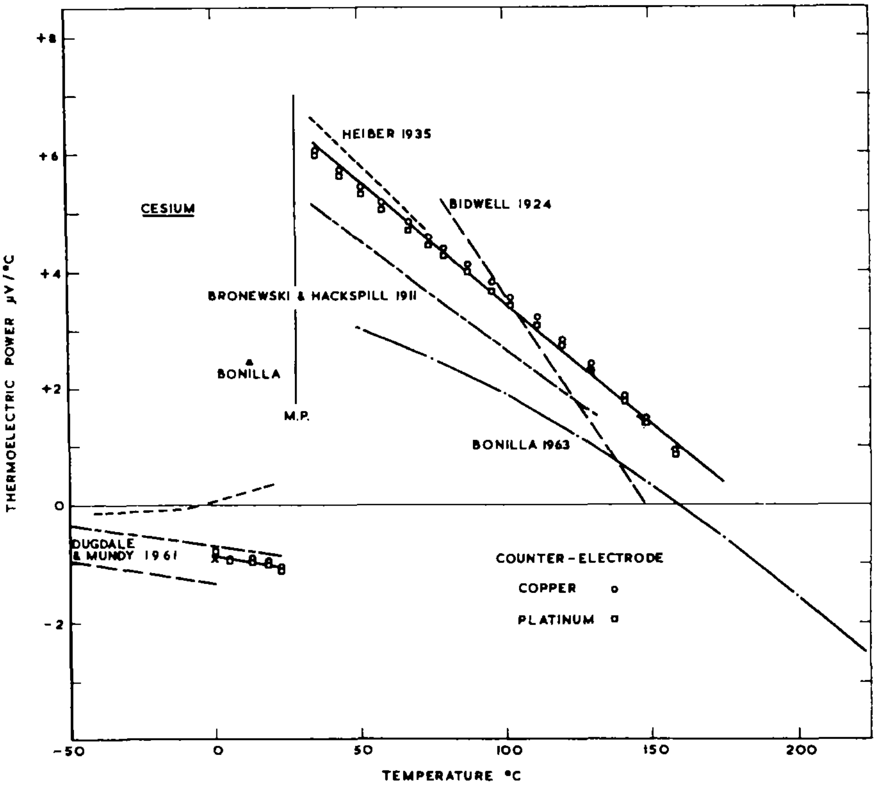

Figure 5. The thermoelectric power of cesium as a function of temperature.

in a stirred cold bath. Readings were taken as the temperature of the lower junction slowly increased from just below 0°C up to room temperature.

The absolute thermoelectric power as a function of temperature is shown in Fig. 5. The agreement between the present results and those of Bonilla *et al.* is poor just above the melting point, but at 150°C the agreement is reasonable and Bonilla's results continue to higher temperatures with a slope very much like that shown by the present results†. As for rubidium the experimental temperature dependence will later be compared with some theoretical values.

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† Professor Bonilla has confirmed that the Pt/Cs data in their table of results should have been given the opposite sign to that for Na, K and Rb.

It can be seen from Fig. 5 that there is a dramatic change in the absolute thermoelectric power of cesium at the melting point; from $-1\ \mu V/^\circ C$ in the solid to $+6.5\ \mu V/^\circ C$ in the liquid according to the present work. The very early measurements by Bronewski and Hackspill substantially agree with this; they found a change from $-1\ \mu V/^\circ C$ to $+5\ \mu V/^\circ C$ on melting. Heiber found a change of $+6.5\ \mu V/^\circ C$ but his sign for the solid had changed from negative to positive just before the melting point. Bidwell's results show a change of approximately $+10.5\ \mu V/^\circ C$.

In contrast to all these large changes the recent measurements by Bonilla *et al.* show very little change at the melting point. In fact, the one value that can be obtained for the solid, $+2.45\ \mu V/^\circ C$, fits in with their values for the liquid so well that it looks as though their cesium was liquid at the reported 25°C. This could be accounted for by a temperature gradient between the cesium and their thermocouple or by contamination of the cesium; the addition of 1 atom% oxygen lowers the melting point of cesium to approximately 25°C.[9]

Lithium

Figure 6 shows the results obtained for solid and liquid lithium, and the only other results that cross the melting point that the author has been able to find in the literature. In the earlier work a quartz tube under oil was used to contain the lithium, whereas in the present work a beryllia tube was used.

The lithium for the present work was obtained from the Foote Mineral Corporation and their analysis showed that the main impurities were potassium 100 p.p.m., sodium 50 p.p.m., chloride 50 p.p.m. and nitrogen 40 p.p.m.; immediately before use the lithium was hot trapped using Zr foil and this would be expected to reduce the nitrogen content.

The apparatus consisted essentially of a 15″ length of 0.186″ O.D. Thermalox 998 tubing that was fitted at each end with thin-wall tubes of tantalum to which the counter-electrodes and thermocouples had been silver-soldered. The tantalum end-pieces were welded to stainless steel tubes that passed through the wall of a surrounding vacuum jacket and led to inlet and outlet valves. The tube was filled with lithium at ~400°C and the first run was made by decreasing the temperature of the upper junction with the lower junction at room temperature. The temperature of the upper junction was then increased and readings were taken on the

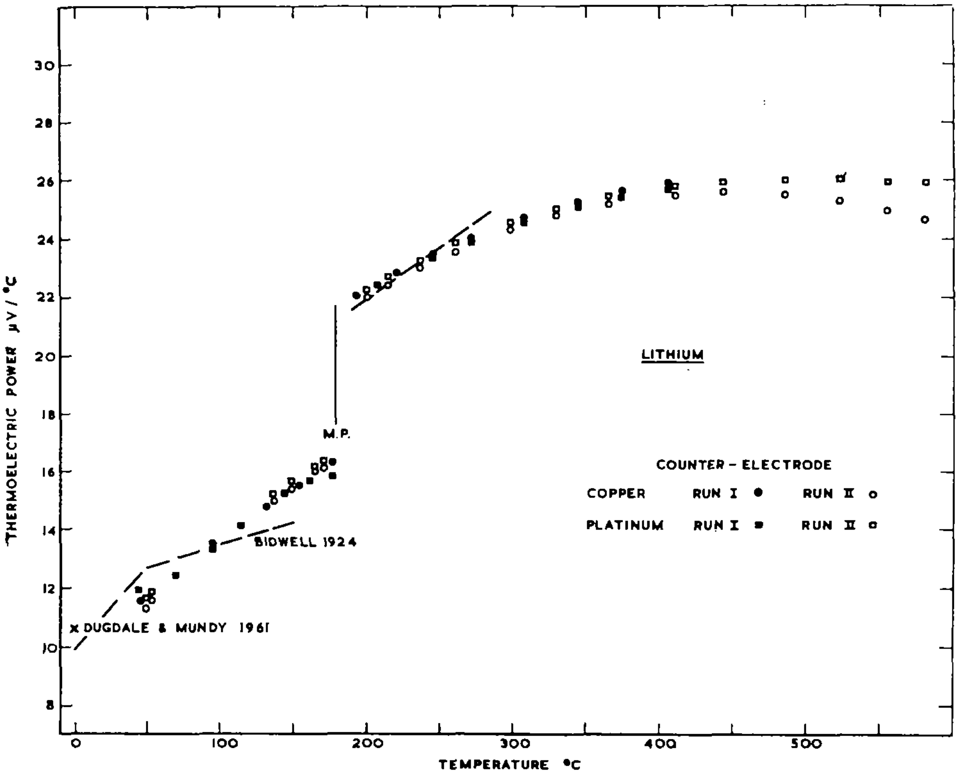

Figure 6. The thermoelectric power of lithium as a function of temperature.

way back through the melting point; these confirmed the value found during the first run for the change on melting. Finally the temperature of the hot junction was taken up to ~600°C and a second run was made down to room temperature. The results of the two major runs are shown in Fig. 6 and they are seen to be in very good agreement over their common temperature range.

The absolute thermoelectric power of lithium is positive in both the solid and liquid states and the change on melting is approximately $+5.5\,\mu V/°C$. Bidwell's values for liquid lithium agree well with the present values and it is reassuring to note that Bidwell stated that "The work on lithium was by far the most satisfactory as regards reproducibility on different runs and with different specimens" since for the other alkali metals Bidwell's values have not been in good agreement with more recent work. The agreement for solid lithium is reasonable, and in particular, as with the other alkali metals, the present measurements on the solid are in accordance with the value for 0°C published by Dugdale and Mundy[10] (1961).

Although the values against copper and against platinum are not in good agreement above 400°C, the high temperature results from run II suggest that the absolute thermoelectric power of liquid lithium may pass through a maximum in the 500°C region and experiments are in hand to investigate this point further.

4. Discussion

The absolute thermoelectric power of a metal can be expressed as

$$S(T) = \frac{-\pi^2 k^2 T x}{3|e|\, E_F} \tag{2}$$

where E_F is the Fermi energy and k Boltzmann's constant, x is a dimensionless parameter which in theory can be obtained from the formula[11],

$$x = E_F \left[\frac{\partial}{\partial E} \log \sigma(E) \right]_{E=E_F} \tag{3}$$

where $\sigma(E)$ is the electrical conductivity for the Fermi surface at energy E.

According to Ziman's theory[1]

$$x = 3 - 2q \tag{4}$$

where

$$q = \frac{|U_{2k_F}|^2\, a_{2k_F}}{\langle U^2 a \rangle} \tag{5}$$

$U(K)$ represents the matrix element of a pseudopotential which is associated with each ion, and $a(K)$ is the structure factor for the liquid. The average function $\langle U^2 a \rangle$ is defined by

$$\langle U^2 a \rangle = 4 \int_0^1 a(K)\, |U(K)|^2 \left(\frac{K}{2k_F}\right)^3 d\left(\frac{K}{2k_F}\right) \tag{6}$$

Where K is the difference between incident and scattered wave vectors. The same average function occurs in the expression for the resistivity,

$$\varrho = \frac{3\pi\Omega}{e^2 \hbar v_F^2} \langle U^2 a \rangle \tag{7}$$

where Ω is the volume per atom and v_F the Fermi velocity.

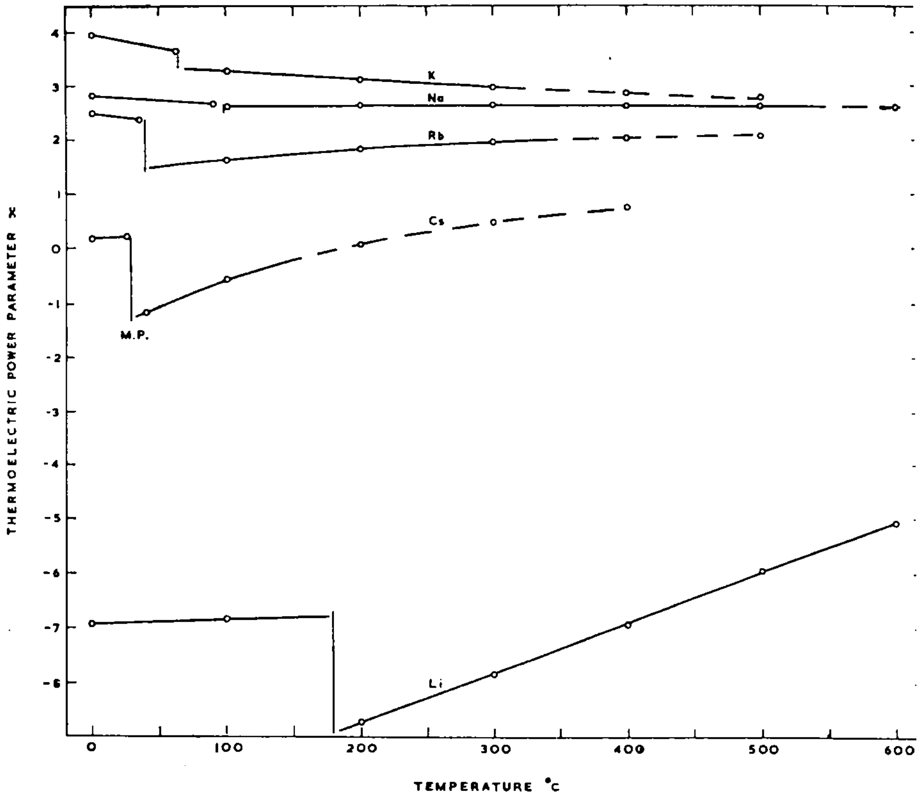

Figure 7. The thermoelectric power parameter x as a function of temperature for the alkali metals.

Since q is always positive x has a maximum value of 3 which should be approached by metals having a small pseudopotential.

A plot of x as a function of temperature, as obtained from the present measurements, is shown in Fig. 7; E_F was calculated from a free-electron expression using densities from various sources including the Liquid Metals Handbook,[12] and the value at 0°C for solid rubidium was obtained from the value for S published by Dugdale and Mundy.[10] It is seen that x for liquid sodium is independent of temperature, having a value of 2.65, whereas x for Rb, Cs, and Li increases with increasing temperature. Potassium is anomolous, as was pointed out by Bradley[2], in that x is slightly greater than 3 in the low temperature part of the liquid range, however, x decreases as the temperature is raised and approaches the value for liquid sodium.

A comparison between results obtained from Ziman's theory and the present experimental results for S is made in Table I. Sundström[13] first calculated S for the liquid alkali metals, using pseudopotentials obtained in the manner of Heine and Aberenkov[14] and structure factors from the neutron diffraction experiments of Gingrich and Heaton.[15] Her results are shown in column 5 and the agreement with experiment is seen to be remarkably good for Na, K, Rb, and Li. However, such good agreement was fortuitous since the theoretical values for S are strongly dependent upon the values used for U_{2k_F}, and the $U(K)$ are not well established. For example, if one uses the Heine-Aberenkov potential as modified by Animalu to allow for non-local screening[16, 17], with the experimental a_{2k_F} as used by Sundström, then the results in column 7 are obtained and it is seen that the agreement with experiment is much less good.

TABLE I A comparison of theoretical and experimental values for the thermoelectric powers of the liquid alkali metals. S is given in μV/°C and the nomenclature follows that used by Ashcroft and Lekner[18]. S_{exp} = present experimental results; $S_{x=3} = S$ obtained by putting $x = 3$; $S_s = S$ Sundström[13] with $U(K)$ Heine-Aberenkov and the experimental $a(K)$; $S_{HA} = S$ obtained using ϱ_{HA}[18], U_{2k_f} Heine-Aberenkov and $a_{2k_f} = 0.8$; $S_A = S$ obtained using ϱ_A[16], U_{2k_f} Heine-Aberenkov-Animalu and the experimental $a(K)$; $S_{HAA} = S$ obtained using ϱ_{HAA},[18] U_{2k_f} Heine-Aberenkov-Animalu and $a_{2k_f} = 0.8$. U_{2k_f} Heine-Aberenkov was calculated from Sundströms' ϱ and S and U_{2k_f} Heine-Aberenkov-Animalu was obtained from the tables quoted by Harrison[20] using the k_F corresponding to the liquid at the melting point. The effective mass has been taken to be unity

Metal	Temp. °C	S_{exp}	$S_{x=3}$	S_s	S_{HA}	S_A	S_{HAA}
Li	180	+21.7	−7.3	+17.7	+14.7	+18.4	+22.1
Na	100	−7.9	−8.9	−8.3	−8.3	−5.3	−3.5
K	65	−14.0	−12.5	−12.0	−11.8	−11.6	−10.3
Rb	40	−6.3	−13.4	−5.7	−10.0	−12.7	−12.7
Cs	30	+6.4	−14.8	−5.6	−9.4	−14.4	−13.9

Some of the disagreement between the theoretical and experimental results may be due to errors in the low K regions of the experimental structure factors. Sundström, for example, observed that if the same $a(K)$, that of sodium, was used for all the alkali metals then the values obtained for the resistivity would be in better agreement with the experimental values, except for Li. A similar result was obtained by Ashcroft and Lekner[18] who calculated structure factors directly from a solution of the Percus-Yevick equation for a hard-sphere model. The structure factors obtained from the model reproduced those from experiment quite well up to and including the first diffraction peak, and the liquid alkali metals were shown to be essentially scaled versions of each other with a_{2k_F}, in each case, in the region of 0.8. If this value is used in conjunction with the values for the resistivities computed by Ashcroft and Lekner for both the Heine-Aberenkov and the Heine-Aberenkov-Animalu model potentials then the values for S shown in columns 6 and 8 are obtained. The results in column 6 show that the improved agreement obtained for the resistivity[16] is not found with the thermoelectric power, and the results in column 8 are in comparatively poor agreement with experiment except for liquid lithium.

One might expect to obtain much better agreement between theory and experiment for the variation of the thermoelectric power with temperature, since this will depend mainly upon the temperature variation of $a(K)$. Sundström[13] calculated values for the thermoelectric powers of liquid rubidium and cesium at various temperatures above those given in Table I but did not compare the results with experimental values. A comparison with the present experimental data—heavily extrapolated for cesium—is made in Fig. 8. The general agreement is seen to be very good for rubidium, and although the calculations give the wrong sign for the region immediately above the melting point they also give approximately the correct variation with temperature for liquid cesium. A value for the variation of the thermoelectric power of liquid sodium with temperature can be obtained from the X-ray diffraction data and theoretical temperature coefficient of resistivity obtained by Greenfield.[19] The agreement between theory and experiment is in fact quite good, but this is not a very exacting test of the theory since the Heine-Aberenkov U_{2k_F} is very small for sodium and good agreement for the temperature variation of S can be obtained merely by putting $x = 3$. Lithium presents a much more interesting case but unfortunately structure factors at more than one temperature are not available at present.

The general conclusion of this work is that relatively small changes in the values of U_{2k_F} could lead to good agreement between theory and experiment for the absolute thermoelectric powers of the liquid alkali

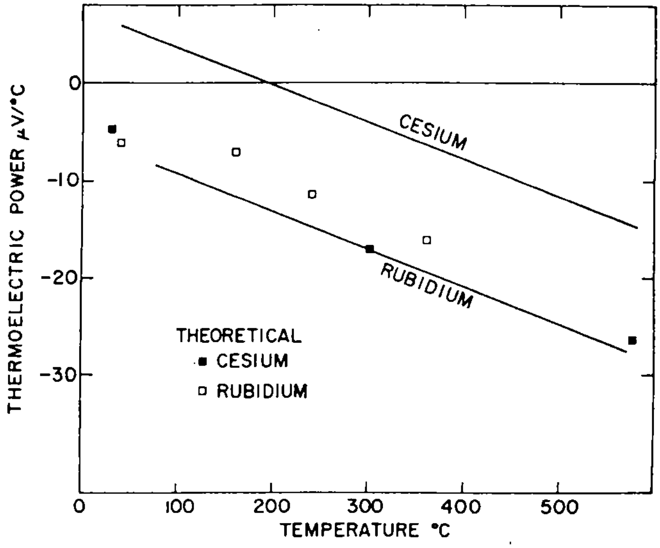

Figure 8. A comparison between Sundströms theoretical values and the present experimental results for the temperature dependence of the thermoelectric powers of liquid rubidium and cesium.

metals. For example, the Animalu and Heine $U(K)$ are reliable to about 0.01 rydbergs[17] and if U_{2k_F} is allowed to vary within this range, while $\langle U^2a\rangle$ remains constant, then for both column 7 and column 8 the resulting ranges in S cover the experimental values except of course for potassium.

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