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A Radiation Balance for the Microcalorimetric Comparison of Four National Radium Standards

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The design of a radiation balance, a twin microcalorimeter utilizing the Peltier effect, to accommodate three Hönigschmid radium standards is described. The rate of energy production of radium and its daughter products down to radium D, for unit mass of radium element in terms of all three Hönigschmid standards, was found to be equal to 138.6 cal g^{-1} hr^{-1}.

1. Introduction

A series of measurements has been completed in which the Canadian national radium standard and the British and United States primary radium standards were compared with each other at the National Physical Laboratory, Teddington, England [1],[1] at the National Research Council's Laboratory, Ottawa, Canada [2], and at the National Bureau of Standards, Washington, D. C. [3].

The measurements at the National Bureau of Standards were made by means of the NBS standard electroscope [4], the radiation balance, and Geiger-Müller and scintillation counters.

The radiation balance already described [5] was far too small to accommodate the large Hönigschmid standards, which are approximately 38 mm long with an external diameter of about 3.5 mm. The Canadian national radium standard is of considerably smaller dimensions, 10.5 mm long and 2.0-mm external diameter, and could be inserted into the cups of the first balance. The radiation balance constructed to accommodate these Hönigschmid standards is described here.

2. Radiation Balance

The radiation balance is a twin microcalorimeter that utilizes the Peltier effect to equalize the temperatures of the two cups. The utilization of Peltier cooling in microcalorimetry, in addition to its use by Callendar [6] and Hoare [7, 8], has also been suggested and used by Duane [9, 10], Tian [11, 12] and and Calvet [13], but none of these authors has used the transfer method of Callendar, which eliminates the necessity for correction for the Joule heating in the Peltier couples and leads. Calvet uses differential systems of two and four cups for the microcalorimetry of slow phenomena, which might not be susceptible to measurement by the transfer method, and Swietoslawski states [14] that Duane considered using a compensating system of two microcalorimeters, but that none of his results is to be found in the literature. It would appear therefore that, apart from the work of Calvet,[2] which uses both the Peltier and Joule effects to compensate the heats of reaction, this method of calorimetry has not hitherto made any great appeal.

The cooling in the radiation balance is applied essentially at a point. It is important therefore not to increase the size of the source containers, or "cups", to such an extent that temperature gradients along them shall be so significant as to cause appreciable differences in heat transfer between each of the cups and their surroundings. It is important that the thermal balance shall be effected chiefly in the material of the cups themselves. In the first balance [5] the cups were copper tubes closed at the lower ends, $^{13}/_{16}$ inch long and having internal and external diameters of 0.099 and 0.130 inch, respectively. This balance had adequate sensitivity for the accurate comparison of radium preparations containing of the order of 5 or 10 mg of radium element. By using gold cups of greater wall thickness it was found possible to improve the thermal mixing in the cups and yet, at the same time, to keep the sensitivity at about the same value.

A new balance was therefore constructed, and is illustrated in figure 1, in which the cups consisted of gold tubes, again closed at the lower ends, each $1^{37}/_{64}$ inch in length and having internal and external diameters of 0.155 and 0.238 inch, respectively. The wall thickness of the gold cups is thus 0.083 inch as compared with 0.031 inch of the copper cups of the original balance. The same type of Peltier couples and thermopile junctions of chromel and constantan were used as before, and, with the same galvanometer and scale position, the sensitivity obtained was 0.21 mm/μw at 25° C as compared with a figure of 0.33 mm/μw at 25° C for the old balance.

Apart from enlarging the copper block containing the radiation-balance cups, the general details of construction were, as can be seen from figure 1, essentially the same as before, and the same auxiliary electrical equipment was also used.

After insertion of the standards to be measured, or of the dummies of the standards, into the cups, silicone oil was used to fill up the cups, which were closed by means of stainless-steel or phosphor-bronze ball bearings $^3/_{16}$ of an inch in diameter.

[1] Figures in brackets indicate the literature references at the end of this paper.

[2] An extensive bibliography is given in [13].

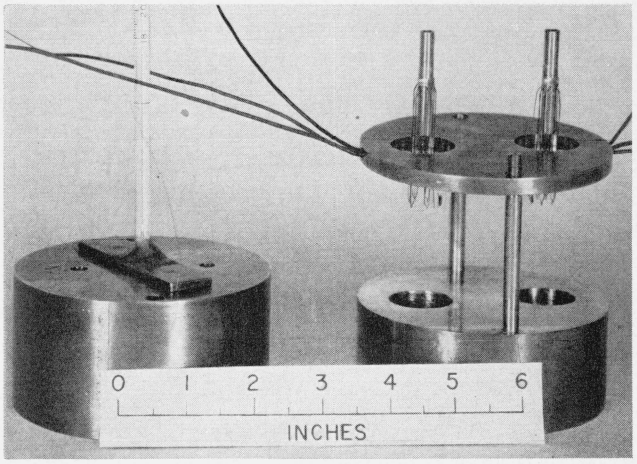

FIGURE 1. *Gold-cup radiation balance.*

3. Theory

If a source A dissipating energy at the rate of W_1 watts in cup 1 of the radiation balance be exchanged with a source B emitting energy at the rate of W_2 watts in cup 2, and if, at the same time, the current, C through the Peltier junctions, which are connected in series, is reversed, then

$$W_1 - W_2 = 2PC + (d_1 - d_2)/s, \tag{1}$$

where P is the Peltier coefficient, d_1 is the galvanometer-scale deflection with A in cup 1 and B in cup 2, and d_2 is the galvanometer-scale deflection with the sources exchanged and the current reversed; s is the galvanometer sensitivity in millimeters per microwatt.

The Peltier coefficient, P, is equal to TdE/dT, where T is the absolute temperature, and dE/dT is the thermoelectric power of the Peltier couple in microvolts per degree. In general, dE/dT is determined at some given temperature and must then be corrected slightly for fluctuations in the ambient temperature. In practice, dE/dT was expressed in microvolts per degree at 25° C and was then corrected by adding or subtracting 0.08 μv/deg C for a chromel-constantan couple for each degree above or below 25° C, the value of dE/dT at 25° C being of the order of 59 μv/deg C. It is also necessary to correct s by the same temperature coefficient in order to allow for the slight change in response at different temperatures of the chromel-constantan couple.

The ratio of the energy dissipations of two sources may, however, actually be determined without measuring dE/dT as eq (1) may be rewritten

$$W_1 - W_2 = \left(2TC + \frac{d_1 - d_2}{s'}\right)\frac{dE}{dT}, \tag{2}$$

where s' is now the scale sensitivity in millimeters per ampère per degree Kelvin, and the source in the second cup is a dummy, i. e., W_2 is equal to zero. As dE/dT at 25° C is a constant of the apparatus, the ratio of the rates of energy production in various radioactive sources can be obtained simply in terms of measurements of current, temperature, and galvanometer-scale deflection. Such ratios are independent of the absolute value of dE/dT, and therefore the uncertainty in the measurement of dE/dT does not enter into such a determination of relative values. Allowance must be made, however, in determining such ratios for the known temperature coefficient of dE/dT in cases where $W_1' - W_2'$ is determined at one temperature and $W_1'' - W_2''$ at another.

As the Peltier effects in each cup will be modified by small losses of heat to or gains from the surroundings, the value of dE/dT that must be used in eq (1) is not, in general, equal to the thermoelectric power of the Peltier couple as determined by the measurement of the variation of electromotive force E as a function of temperature T. It is necessary therefore to determine the *effective* value of dE/dT by means of a heating coil, together with a compensating coil, which can be placed inside the two cups. In this calibration it should not be necessary exactly to reproduce in the heating coil the dimensions of the radioactive source, provided the cups are of such dimensions, and of material of sufficiently good thermal conductivity, that large differences of temperature cannot be maintained and that good thermal "mixing" results.

In actual practice, the value of dE/dT for the chromel and constantan wire used in both the old balance [5] and that described here was found to be approximately 61 μv/deg C, by direct measurement, whereas the calibrated values for both balances gave a value of dE/dT of about 59 μv/deg C (59.11 for the old [5] and 58.78 for the new, which has larger cups).

4. Calibration of the Radiation Balance

In view of the large differences in dimensions of the Hönigschmid radium standards, on the one hand, and the Canadian national standard, on the other (see fig. 2), it was felt desirable to use two sets of calibration coils, one set simulating the Hönigschmid standards and the other simulating the smaller Canadian standard. These are also shown in figure 2. The resistances of these coils were measured after the calibration experiments in the radiation balance had been carried out in order not to impair the insulation of the leads to the coils, which had to be bared in order to attach potential leads of 38-gage constantan wire. On both sets of coils these potential leads were attached with an accuracy of about ±0.1 mm to points on the coil leads approximately 5 cm and then 4 cm from the ends of the coils that rested on the bottoms of the radiation-balance cups when the coils were inserted into them. If R be the resistance of the main coil of either set, r the resistance of the compensating coil, i the current in the coils in series, and C the current in the Peltier junctions in series, then on interchanging the coils between cup 1 and cup 2 and reversing the Peltier

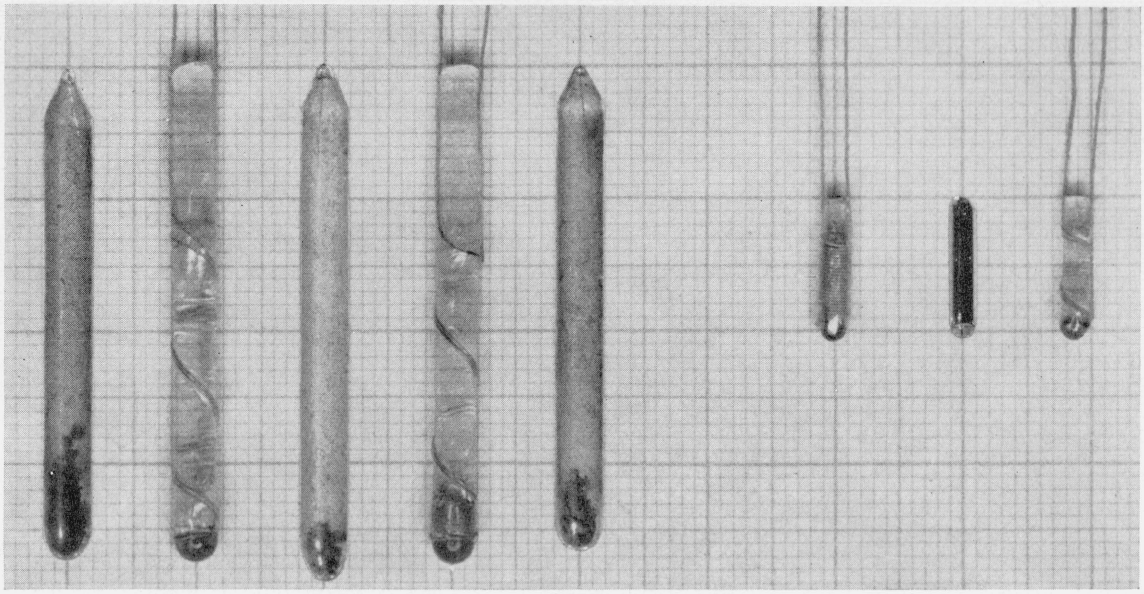

FIGURE 2. *Four national radium standards and the corresponding calibrating coils.*

Left to right: United States primary radium standard, 5437, XIV, compensating "Hönigschmid" coil; British primary radium standard, 5432, main "Hönigschmid" coil; United States primary standard, 5440, XV, main "Canadian" coil; Canadian national standard, XIII, compensating "Canadian" coil. The scale shown is in millimeters.

current, C, we have

$$i^2(R-r)=W_1-W_2$$
$$=\left(2TC+\frac{d_1-d_2}{s'}\right)\frac{dE}{dT}$$

whence

$$\frac{dE}{dT}=\frac{i^2(R-r\ )}{2TC+(d_1-d_2)/s'}. \qquad (3)$$

As $(d_1-d_2)/s'$ is usually small compared with $2TC$ it is sufficiently accurate, in deriving dE/dT, to use s as a first approximation, and to derive a slightly more accurate value as a second approximation.

The values obtained for the resistances of the calibrating coils, when compared by means of a potentiometer with a 10-ohm standard coil, are shown in table 1. The results obtained by balancing the Peltier cooling against the Joule heating of the calibrating coils are given in table 2.

The average values for dE/dT, using the results shown in tables 1 and 2, are 58.91 μv/deg C for the "Hönigschmid" coils and 58.64 μv/deg C for the "Canadian" coils. The average of these is 58.78 μv/deg C.

The difference between the results for the two coils is not considered to be outside the experimental error for this particular calibration. The nearer to a point source of radiation to which one approximates, the more effective will the Peltier cooling become, so that one might expect the Canadian coils to give, if anything, a larger value for dE/dT. That the reverse is the case would support the idea that the difference is experimental.

TABLE 1. *Resistance of calibrating coils*

Coils	Distance of potential leads from ends of coils (cm)	Current (amp)	R (Ohms)	r (Ohms)	$R-r$ (Ohms)
"Hönigschmid"	5.20	0.017730	12.807_8	7.710_9	5.096_9
	5.20	.031150	12.807_4	7.712_5	5.095_0
	4.30	.031165	11.732_0	6.611_6	5.120_4
	4.30	.017733	11.733_1	6.613_3	5.119_8
"Canadian"	4.90	.018261	15.574_5	6.878_1	8.696_4
	4.90	.032801	15.573_9	6.877_7	8.696_2
	3.80	.032779	14.263_8	5.563_7	8.700_1
	3.80	.018256	14.264_3	5.564_0	8.700_3

TABLE 2. *Calibration of the radiation balance*

Coils	Current in coils (amp)	Balancing Peltier current (amp)	Residual galvanometer deflection on transfer (mm)	Temperature (° C)	$\frac{dE/dT}{R-r}$ (μv deg^{-1} ohm^{-1})
"Hönigschmid"	0.022427_5	0.074828_5	11.1	24.5_5	11.518
	.016478	$.039560_5$	0.15	24.4_7	11.534
"Canadian"	$.023300_5$	.135989	1.35	23.5_5	6.736
	$.016940_3$	$.071418_3$	−3.35	23.7_3	6.724

To obtain double assurance on this point, however, a 4.98-mg radium preparation in a platinum-iridium needle 15 mm in length was measured both in the old [5] and in the new radiation balances. It was then encased in a glass tube of the same dimensions as the Hönigschmid standards and remeasured in the new balance. In the first measurements the platinum-iridium needle was entirely immersed in silicone oil in the cups of the old and the new balances. In

the glass tube it had air around and above it, so that the temperature distribution should have approximated that pertaining for the Hönigschmid standards. The platinum-iridium needle used was radium source number 35917 referred to in Research Paper 2486 [5].

The value for the energy absorbed from radium source 35917 in the old radiation balance, corrected for the growth of polonium-210, was 747.3 μw, compared with 746.3 μw previously obtained [5]. The values in the new balance, both unsheathed and sheathed in a 38-mm long glass tube of 3.1-mm internal diameter, and corrected for the growth of polonium-210 and to the equivalent in gamma-ray absorption of the old balance, were, respectively, 749.8 μw and 749.1 μw. The difference between these two values is insignificant.

5. Experimental Results

During the first week of February 1954 the radiation balance was used to determine the rate of energy production of four national radium standards. The results of these measurements have already been reported in detail [3]. In addition to these results it is, however, possible to derive a new value of the rate of energy production per milligram of radium element using the masses of the three standards that were determined by Hönigschmid on June 2, 1934. The mass of radium element in the Canadian standard is only a derived mass based on comparisons with the 1911 Paris and Vienna standards, and it is, moreover, doubtful if any absorption correction was made in those comparisons. Only the masses determined by direct weighing by Hönigschmid have therefore been used in a redetermination of this constant for radium.

The masses of radium element in the three primary standards as determined by Hönigschmid on June 2, 1934, and also the same masses corrected to February 2, 1954, using a half-life of 1,620 years, are shown in table 3, together with the rate of energy absorption as determined by the radiation balance and the ratio of energy absorption in microwatts to mass of radium element in milligrams on February 2, 1954.

The average value of the ratio of the rate of energy absorbed in the radiation balance to the mass of radium element, obtained by dividing the sum of all three rates of energy absorption by the sum of all three masses is 165.83 μw/mg of radium element, the standard deviation of the individual results being 0.13 percent.

Using the expression derived by Curie and Yovanovitch [15], and later modified by Sanielevici [16] and Jordan [5], the growth of polonium-210 in 19⅔ years, from June 1934 to February 1954, is calculated to give rise to a rate of energy production equal to 13.6_0 μw/mg of radium element. The corresponding energy increment due to radium E is 0.87 μw/mg of radium element. Hence the ratio of rate of energy production to mass becomes 151.36 μw/mg of radium element, when corrected for the growth of polonium-210 and of radium E, or 130.20 cal g^{-1} hr^{-1} (all the polonium-210 alpha particles and radium E beta particles being absorbed).

TABLE 3. *Results for three national primary radium standards*

	British primary radium standard (5432)	U. S. primary radium standard (5440, XV)	U. S. primary radium standard (5437, XIV)
Mass, in milligrams, of radium element June 2, 1934	15. 60	20. 45	38. 23
Mass, in milligrams, of radium element February 2, 1954	$15. 46_9$	$20. 27_9$	$37. 91_0$
Rate of energy absorption, in microwatts	2569. 8	3360. 7	6293. 4
Microwatts per milligram of radium element	166. 01	165. 60	165. 89

This result was, however, obtained with gold cups and glass tubes that together have a gamma-ray absorption equivalent to only 0.184 cm of lead. Approximately 7 percent of the energy dissipation of radium occurs in the form of gamma radiation, the absorption of which has been measured calorimetrically by Zlotowski [17] up to an equivalent of 8 cm of lead, at which thickness of absorber the curve is essentially flat [5].

Using Zlotowski's absorption curve, the value of 130.20 cal g^{-1} hr^{-1} for absorber equivalent to 0.184 cm of lead can be corrected to "infinite" thickness of absorber; i. e., to an absorption equivalent to 8 cm of lead. A value of 138.6 cal g^{-1} hr^{-1} is then obtained.

The value of 130.20 cal g^{-1} hr^{-1} is estimated to have an accuracy of ± 0.5 percent. The standard deviation of the individual results is, however, as low as 0.13 percent. Sources of radiation can therefore be compared with each other with a greater accuracy than their absolute energy emission can be measured, on account of the greater uncertainty in the determination of the effective value of dE/dT.

The old radiation balance [5] gave a value for this ratio of 128.9 cal $g^{-1}hr^{-1}$ for 0.126 cm of lead equivalent,[3] which becomes 137.5 cal g^{-1} hr^{-1} when corrected to an absorption equivalent to 8 cm of lead. This value was obtained, however, using needles whose radium content had been determined by gamma-ray comparison with the United States primary radium standard and not directly by weighing. The result obtained by Zlotowski [17] was 139.6 cal g^{-1} hr^{-1} for an absorption equivalent to 8 cm of lead.

[3] The value quoted [5] was 128.9 cal g^{-1} hr^{-1} but this becomes 128.8 cal g^{-1} hr^{-1} when the small radium E correction is included.

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