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AN INVESTIGATION OF ANOMALOUS THERMAL POWER GENERATION FROM A PROTON CONDUCTING OXIDE

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ABSTRACT

A high-temperature Seebeck effect calorimeter, in which the thermoelectric emf across a large-area enveloping thermopile is a measure of the heat flux from a power source, has been constructed to examine the claimed generation of excess thermal energy from a proton-conducting oxide immersed in deuterium gas. The claim has been confirmed in a few experiments out of many unsuccessful ones.

INTRODUCTION

Beginning with the initial work of Pons and Fleischmann (1), a number of reliable calorimetric determinations have been carried out (2,3) that have demonstrated that in a variety of processes it is possible to obtain more thermal power than can be accounted for by the electrical power put into the system. The most careful calorimetric work of this kind has been done on the cathodic deposition of deuterium upon palladium. Because the First Law of thermodynamics is still regarded as inviolate, the generation of the additional power has been inferred to arise from some as-yet unknown nuclear process, and the field has acquired the label "cold fusion". It is also true that many investigators, some working very carefully, have not been able to detect any "excess power", and indeed the investigators who have reliably demonstrated the development of excess power in some experimental runs often fail to replicate those results in subsequent experiments. This irreproducibility, plus the inexplicability of the generation of power via nuclear reactions as they are currently understood, are the cause of the skepticism and outright hostility that the field of "cold fusion" has engendered.

At the Fourth International Conference on Cold Fusion, T. Mizuno (4) announced the generation of excess thermal power from a perovskite oxide held in deuterium gas at temperatures about 400°C (see also (5)). In these experiments the oxide specimen bathed by D₂ gas is maintained at the desired temperature by measured, constant electrical power delivered to a small furnace inside of a gas tight enclosure. Then a voltage whose polarity is alternated at a

frequency between 10^{-4} and 1 Hz is applied across the specimen thickness, generating a small, measured electrical power in the specimen. In some, but not all such experiments (about 12 out of 80 attempts), the specimen temperature was observed to rise considerably above the value consistent with the electrical power furnished to the specimen.

Because thermal power generated at high temperatures can be converted to other forms of power with greater Carnot efficiency than thermal power at lower temperatures, Mizuno's generation of excess power is particularly interesting. In addition, Biberian (6) following earlier work by Forrat (7) has also claimed to have generated excess power with LaAlO_3 in D_2 gas by a similar process. For these reasons it has seemed important to attempt to verify claims of the production of excess power from perovskite oxides. The present work has been done with specimens of nominal composition $\text{SrCe}_{0.9}\text{Y}_{0.08}\text{Nb}_{0.02}\text{O}_{2.97}$ made and supplied by Dr. T. Mizuno of Hokkaido University.

EXPLORATORY EXPERIMENTS

Our early work with Mizuno's specimens was carried out with an isoperibolic type calorimeter which employed the temperature rise, measured by a chromel-alumel thermocouple, as the indicator of the power generated within the reactor. The apparatus was first calibrated without a specimen in place and with deuterium gas in the reactor, using a small furnace and an auxiliary heater to furnish power. The result was a linear plot of thermocouple emf vs. input power. The apparatus was then dismantled, a perovskite disc was installed and the apparatus was reassembled. After evacuation and heating to the desired temperature between 360 and 410°C, D_2 gas was admitted and thermal stability was allowed to be attained at constant power input. After this direct current, the polarity of which was periodically alternated by a simple timer-relay, was supplied to the specimen. Again thermal stability was awaited. The temperature attained was then compared with that given by the calibration line for the same total power input. In some infrequent instances the temperatures reached higher values with the specimen than those consistent with calibration line.

However, two problems prevented verification of excess power generation with the isoperibolic calorimeter. It was found that the steady state thermocouple reading produced by a given electrical power to the furnace was about 5° lower than that produced when the same total power was shared between the furnace and the auxiliary heater. This effect undoubtedly due to the different spatial distribution of power sources cast serious doubt on the putative excess power generation since furnishing alternating d.c. power to the specimen necessarily produced a spatial distribution of input power different from that during calibration. The second problem discovered was that a change in the composition of the gas phase within the reactor causes a significant change of steady-state temperature. Specifically admission of a small amount of air, either wittingly or unwittingly by an air leak or by outgassing of the ceramic of the furnace, causes an increase of temperature at constant power input. Surprisingly, adding N_2 and O_2 molecules to a constant number of D_2 molecules decreases the thermal conductivity of the gas despite the larger number of thermal carriers thereby introduced.

For these reasons isoperibolic calorimetry was abandoned and a Seebeck, or heat-flow, calorimeter was designed and built.

THE SEEBECK CALORIMETER

The principle of Seebeck calorimetry is the generation of a thermoelectric emf by a large number of thermocouple junctions connected in series in response to a temperature difference, ΔT , across the walls of an enclosure that totally surrounds a source of thermal power. The multiple thermocouples are arranged such that junctions of one polarity lie on the outside surface (that contacting a heat sink) of the enclosure, and junctions of the opposite polarity lie on the inside surface of the enclosure. If the thermocouple junctions completely and densely surround the source of thermal power and the thermal conductivity of the material of the enclosure is K , the thermal power transmitted to the constant temperature heat sink is $P_{\text{out}} = K\Delta T$, where ΔT is the average temperature difference across the enclosure walls as integrated by the multiple thermocouples, and at steady state $P_{\text{out}} =$ thermal power generated within the enclosure. In practice it is, of course, impossible to cover the entire wall area of the enclosure since power leads, gas ducts, etc., must have access to the interior of the enclosure. Hence, in general at steady state $P_{\text{source}} = P_{\text{out}} = K\Delta T + a(T_i - T_s) + b(T_i - T_L)$, where T_i , T_s , and T_L are the temperatures of the source, the heat sink, and the laboratory, respectively. With proper design, the second and third terms can be rendered small, and the relation between P_{source} and the Seebeck signal, E_s , (which is linear in ΔT) can be established by calibration by using a known heat source.

CONSTRUCTION OF THE SEEBECK CALORIMETER

The apparatus consists of three principal units. These are a gas-tight envelope for the specimen and furnace, the Seebeck thermoelectric device, and the thermostatted environment (Fig. 1). These are discussed separately.

The envelope (the reactor) for the specimen is a stainless steel closed cylinder welded to a stainless steel flange which mates via a copper gasket with another stainless steel flange through which enter the power leads for the small furnace that surrounds the specimen, and for the specimen and for an auxiliary heater, as well as a chromel-alumel thermocouple and a stainless steel tube which leads via swagelock fittings to a vacuum and gas-handling system made entirely of metal. The perovskite disc specimen, sandwiched between either thin palladium or platinum discs, is supported by perforated copper plates within the furnace made of nichrome wire wound on a spirally grooved ceramic tube. The specimens supplied by Dr. T. Mizuno measure about two cm in diameter by about 1 mm in thickness. The faces of the disc have been thinly coated with metal, either Pd or Pt Mo. Within the furnace is also a small coin-shaped ceramic cast about a spirally wound nichrome wire made and supplied by Mr. Jeff Driscoll. This device serves as an auxiliary heater used for calibration of the calorimeter. The junction of the chromel-alumel thermocouple is in the gas phase between the specimen and the inside of the furnace tube.

The Seebeck calorimeter itself is a parallelepiped enclosure made of machineable ceramic, and it surrounds the reactor on five sides. The sixth side, its base, rests on insulating ceramic. Through 1/16 inch diameter holes in each of the five sides a continuous wire of

alternating chromel and alumel segments is threaded in such a way that the inside surface of the ceramic parallelepiped has 355 thermoelectric junctions and the outside surface has an equal number of junctions of opposite polarity. The thermoelectric emf developed by the temperature difference between the inside and the outside surfaces, integrated over the five sides, is measured both by a digital millivoltmeter and by a sensitive strip chart recorder. The latter continually records the difference between the thermoelectric emf and an applied adjustable constant voltage in order to increase the sensitivity of the recorder to small variations of the thermoelectric emf. The purpose of the strip chart recorder is to have a record of the time dependence of the thermoelectric signal, E_s . About 5 hours are required to attain steady state (Fig. 2). Because of the greater sensitivity of the digital voltmeter, its readings of E_s at steady state are taken for plots of E_s vs. input power and subsequent analysis.

At steady state, that is when temperatures everywhere in the system are time independent, the thermoelectric emf is a measure of the power generated within the reactor. Clearly this necessitates a time-independent temperature of the environment that serves as a heat sink. This is accomplished by an insulated cylinder that envelopes the Seebeck calorimeter. It is fitted with a large-area heater and an air fan driven by a constant-speed motor. The average temperature of the air within this insulated jacket is maintained constant by a controller, operating between two adjustable power levels, which uses the output of four thermocouples connected in series as the distributed sensing element. In order to make the Seebeck calorimeter less sensitive to fluctuations in air movement between regions of different temperatures, the Seebeck box is closely surrounded by a five-sided enclosure made of copper sheet which causes the Seebeck system to "see" the average temperature of the circulating air.

All wire connections and the tube for evacuation of the retort and admission of gases to it are led out below the retort through an opening in the insulated platform that supports all of the systems described above. The platform in turn is supported by a stand which is entirely surrounded by an insulating skirt. A constant-current d.c. power supply furnishes power to the furnace within the retort. Separate d.c. power supplies furnish power to the auxiliary heater and to the specimen. In all cases the power delivered is measured by digital ammeters and voltmeters, taking care that the same instruments and settings are used both in calibrations and in the experimental runs. The signal from the thermocouple within the reactor is read by a digital millivoltmeter. The temperature of the circulating air is continuously recorded and also occasionally measured by a hand-held Fluke voltmeter.

Calibration of the calorimeter is accomplished by furnishing measured electrical power to the furnace and to the auxiliary heater and measuring E_s at steady state. By varying the ratio between the power supplied to the furnace and that supplied to the auxiliary heater it was verified that E_s is independent of the spatial distribution of the power sources, whereas the reading of the internal chromel-alumel thermocouple depends upon that distribution. The calibration is found to yield a linear E_s (P) relation, where P is the total input power. Furthermore, the E_s (P) relation does not depend on the thermal conductivity of the gas within the reactor (Figure 3), whereas the reading of the internal thermocouple is a strong function of the nature of the gas phase.

RESULTS AND DISCUSSION

The initial experiments with the Seebeck calorimeter were done by first establishing the E_s (P) relation with D_2 gas without the perovskite specimen in place. The reason for this precaution is that in earlier work with the isoperibolic calorimeter some results seemed to show generation of excess power before d.c. power was supplied to the specimen. After calibration without the specimen, the specimen was put in place within the reactor, the apparatus was reassembled and an experimental run was carried out. Generation of excess power is judged by comparing the E_s produced by a given value of P with the E_s value given by the calibration line for that value of P. The experimental run with a specimen in the reactor consisted of heating the reactor by means of the furnace while continually evacuating the reactor by means of a mechanical pump. After reaching a temperature in excess of 400°C deuterium gas was admitted to a pressure between 0.1 and 0.3 atm and a steady state was allowed to be attained. Direct current of alternating polarity was then applied to the specimen and steady state was again awaited. The frequency of alternation of polarity was between 0.1 and 0.003 Hz. The temperature of the air surrounding the Seebeck box was maintained constant at 106°C .

Many experiments were done in this fashion while the performance of the calorimeter was continually improved. Although some indications of the generation of excess power were obtained during this period none can be considered reliable. Final modifications of the calorimeter produced reliable operation, as shown by Figure 2. At this stage an experiment was carried out which appears to have yielded excess power (Experiment X). First a calibration was carried out, without the specimen in place, with deuterium gas in the reactor. Then the apparatus was totally disassembled, re-assembled and another calibration, again without a specimen in the reactor, was made. The two calibrations for E_s (P) agree with each other and can be fitted by a straight line characterized by $r = 0.9988$ and standard deviation $\sigma = 0.116$ mV. A perovskite specimen was then mounted within the reactor and an experimental run at about 410°C was carried out which is detailed in Table 1. The first point established without d.c. current into the specimen falls within one standard deviation from the calibration line, giving confidence that the calibration is valid for the experiment with the specimen in place. After this, 0.009 W of d.c. power with its polarity alternating at about 0.008 Hz was supplied to the specimen; the power to the furnace was adjusted attempting, unsuccessfully, to keep the total input power constant. This produced an E_s value above the calibration line, and the positive deviation persisted after the d.c. power to the specimen was turned off. After this, the experiment was continued at times with, and at other times without, d.c. power to the specimen. The steady-state points are all considerably above the calibration line. One can have considerable confidence that the six data points in Table 1 that lie at more than four sigma values above the calibration line exhibit the generation of excess power. For orientation, a deviation, δ , of +0.6 mV represents excess power equal to 0.65 W which is considerably larger than the d.c. power into the specimen ranging from 0.047 to zero watt. Fig. 4 displays the values of excess power calculated from the positive deviations from the calibration line. The episodes characterized by more than 4σ deviation from the calibration line produced excess power over a cumulative time of 90 hours.

During the period leading to the successful experiment described above it was noted that now and then an E_s (P) calibration was obtained after a disassembly/re-assembly sequence that was somewhat different from what had been obtained prior to that operation despite great care to reproduce exactly all features of the assembly. To avoid this possible source of uncertainty, it was decided to calibrate with a specimen already within the reactor, but using helium within the reactor to avoid the possible generation of excess power during calibration. Then without

disturbing the apparatus the helium was evacuated and replaced by deuterium for the search for excess power generation.*

Six experiments were carried out as described, each one with a calibration using helium for which the deviations from the respective regression lines were calculated. The distribution of these deviations characterized by the number, n , of sigmas is shown in Table 2 in which the calibration data of experiment X are also included for completeness. The distribution is roughly Gaussian. Table 2 also displays the distribution of n -values for the power runs with deuterium of the six determinations that had been preceded by calibrations with helium, as well as for the data of Table 1. It is noted that all but one entry represent positive deviations, and that the distribution is heavily weighted toward large values of n . Most of the large values arise in two experimental runs, the one labeled X and detailed in Table 1, and run B, detailed in Table 3, from the sequence of six experiments that employed helium for the calibrations. Figure 5 displays the values of excess power calculated from the positive deviations given in Table 3. Again, we pay attention only to the data characterized by more than 4σ deviation from the calibration line and note that excess power can be developed even without alternating d.c. power into the specimen. It is worthwhile to remark that the same perovskite specimen was used in experiment X (Table 1) first, then later in experiment B. This specimen was coated by Dr. Mizuno with 300 nm of platinum by sputtering. It is also worth recording that run B developed excess power only after some days during which the determinations were on the calibration line, after which a lengthy, high-temperature continuous evacuation of the reactor and heating of the vacuum lines were carried out. After obtaining the data given in Table 3 for Run B, the calorimeter was calibrated again with the specimen undisturbed in place and under helium, yielding points on the same calibration line as before.

These data provide strong evidence that under some conditions this strontium-cerium based oxide in an atmosphere of deuterium gas can produce thermal power, as claimed by Mizuno and collaborators. However, it is clear that the ratio of experiments with which success in generating excess power can be claimed to those which yield only points lying on the calibration line is small. Mizuno et al. have reported a similar experience. The factors that lead to this lack of reproducibility are unknown, but it is suspected that they are related to details of specimen preparation. In the present experiments much variation among the specimens was noted in the electrical resistance across the thickness of the specimens as well as of the faces of the discs, and also in the appearance of the metallic coatings on the disc faces. It is believed that success in developing reproducibility depends on learning how to produce the required characteristics in the perovskite, whether these be composition, dopant distribution, crystallite size, grain boundary structure and composition, etc. It is emphasized that the calorimetric method employed in this kind of work should not depend upon a measurement of temperature because the thermal conductivity of the ambient gaseous phase depends markedly upon its composition and this can change in the process of experimentation, leading to incorrect conclusions.

The magnitude of the thermal power generated in these experiments is small and clearly not interesting from a technological point of view. However, at the present stage establishment of the phenomenon is important. Much work is needed to increase the reproducibility and the

* I am indebted to my son, Steven R. Oriani, for suggesting this procedure.

power output, as well as to achieve understanding of the mechanism which is currently completely mysterious.

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TABLE 1

Details of Experiment X

d.c. power W	P, Total Input Power, W	E_s , mV	Duration of episode, h	δ , mV	n
0	65.20	73.60		+0.11	1
0.009	65.14	73.75		+0.32	2.7
0	64.83	73.72	17	+0.57	4.9
0.015	64.765	73.75	7	+0.66	5.7
0	64.77	73.74	16	+0.65	5.6
0.036	64.656	73.63	10	+0.64	5.5
0	63.44	72.12		+0.24	2.1
0	66.88	75.55	23	+0.52	4.5
0	68.22	76.61		+0.36	3.1
0	68.31	76.63		+0.30	2.6
0.039	68.36	76.67		+0.29	2.5
0.047	68.18	76.74	17	+0.52	4.5

Notes: E_s = Seebeck emf

δ = deviation of measured E_s from E_s calculated from regression line, $E_s = 13.187 + 0.9152 P$, for the calibration specific to this experimental run, for which $r = 0.9988$ and $\sigma = 0.116$ mV.

$n = \delta/\sigma$

The tabulated numbers are listed in the order of experimental measurement.

TABLE 2
Distributions of n values ($n = \delta/\sigma$)

For Power Experiments of Runs X and B			
n-values	all calibration points	Experiment X	Six D ₂ runs
7.0 to 7.5			2
6.5 to 7.0			
6.0 to 6.5			
5.5 to 6.0		3	
5.0 to 5.5			
4.5 to 5.0		2	1
4.0 to 4.5			1
3.5 to 4.0			1
3.0 to 3.5		1	2
2.5 to 3.0		3	
2.0 to 2.5		1	4
1.5 to 2.0	1		2
1.0 to 1.5	5	1	4
0.5 to 1.0	5		4
0 to 0.5	10		5
-0.5 to 0	6		
-1.0 to -0.5	6		1
-1.5 to -1.0	2		
-2.0 to -1.5	4		

Notes: The second column refers to the data points of eight calibration runs. The third column refers to the data points (episodes) of power run X which followed two calibration runs using D₂ gas without the specimen in place. The fourth column refers to data points (episodes) of the six power runs each of which was preceded by a calibration run using He gas with the specimen in place.

TABLE 3

Details of Experiment B

d.c. power, W	P, total power, W	E_s , mV	Duration of episode, h	δ , mV	n
0	72.11	77.31		+0.073	1.3
0.25	72.49	77.61		+0.086	1.5
0.25	72.60	77.61		+0.003	0.05
0	79.423	82.87		+0.125	2.2
0.399	79.896	83.33	16	+0.229	4.1
0.432	79.876	83.49	24	+0.404	7.3
0.484	79.903	83.50	25	+0.393	7.1
0	79.40	82.98	16	+0.252	4.5
0	79.40	82.78		+0.052	0.9

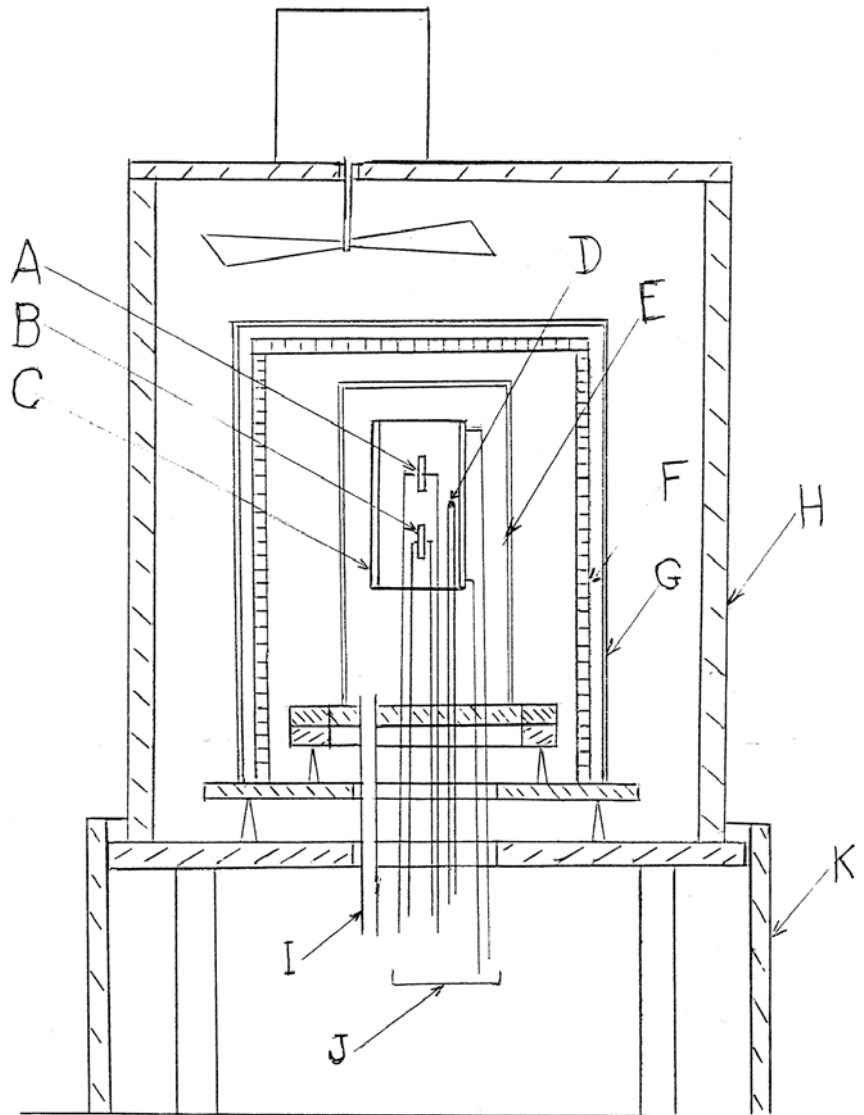
Notes: E_s = Seebeck emf

δ = deviation of measured E_s from E_s calculated from regression line, $E_s = 22.93 + 0.75312 P$, for the calibration specific to this experiment, for which $r = 0.99982$ and $\sigma = 0.0556$ mV.

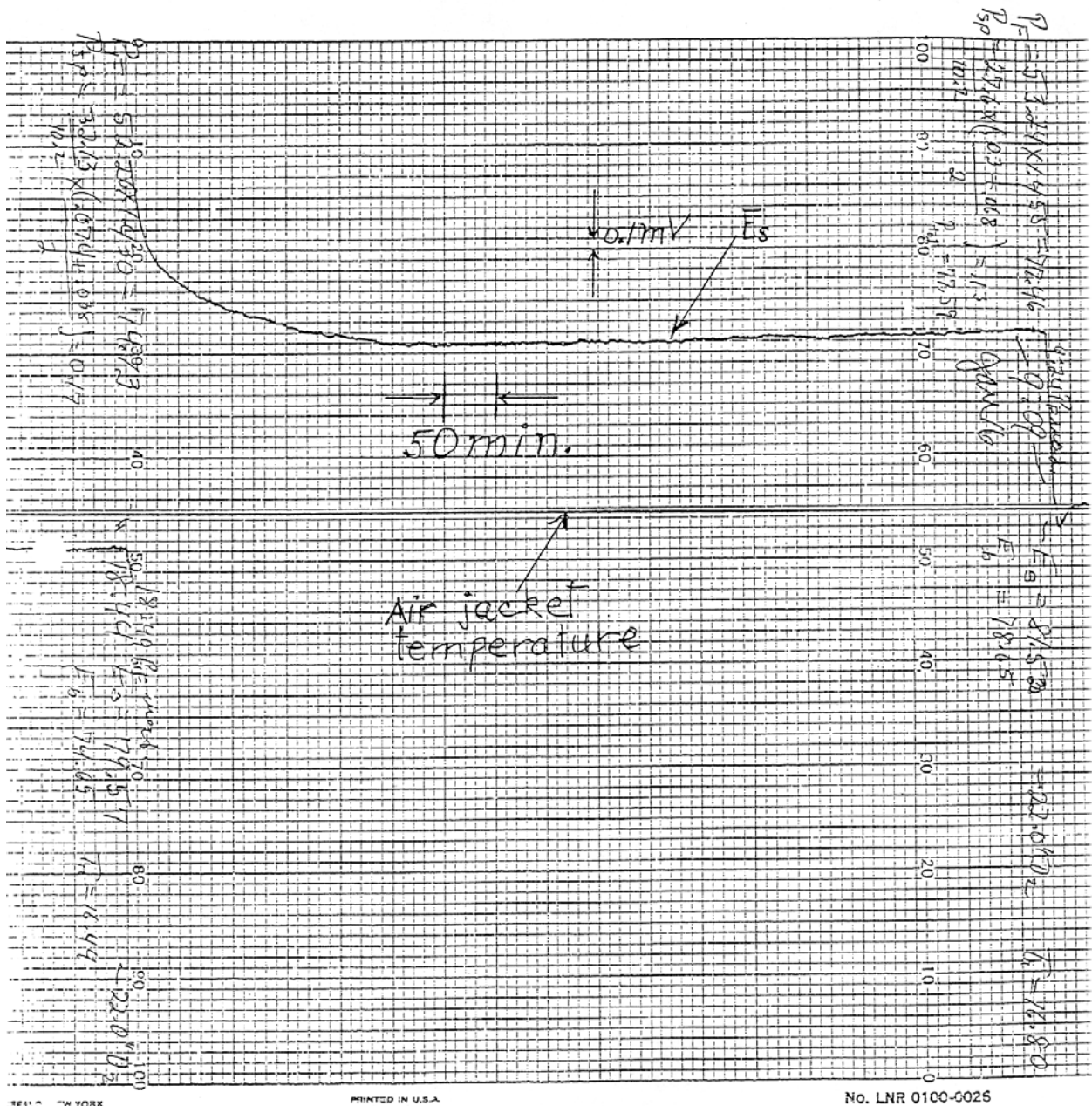
$n = \delta/\sigma$, where $\sigma = 0.0556$ mV.

The tabulated numbers are listed in the order of experimental measurement.

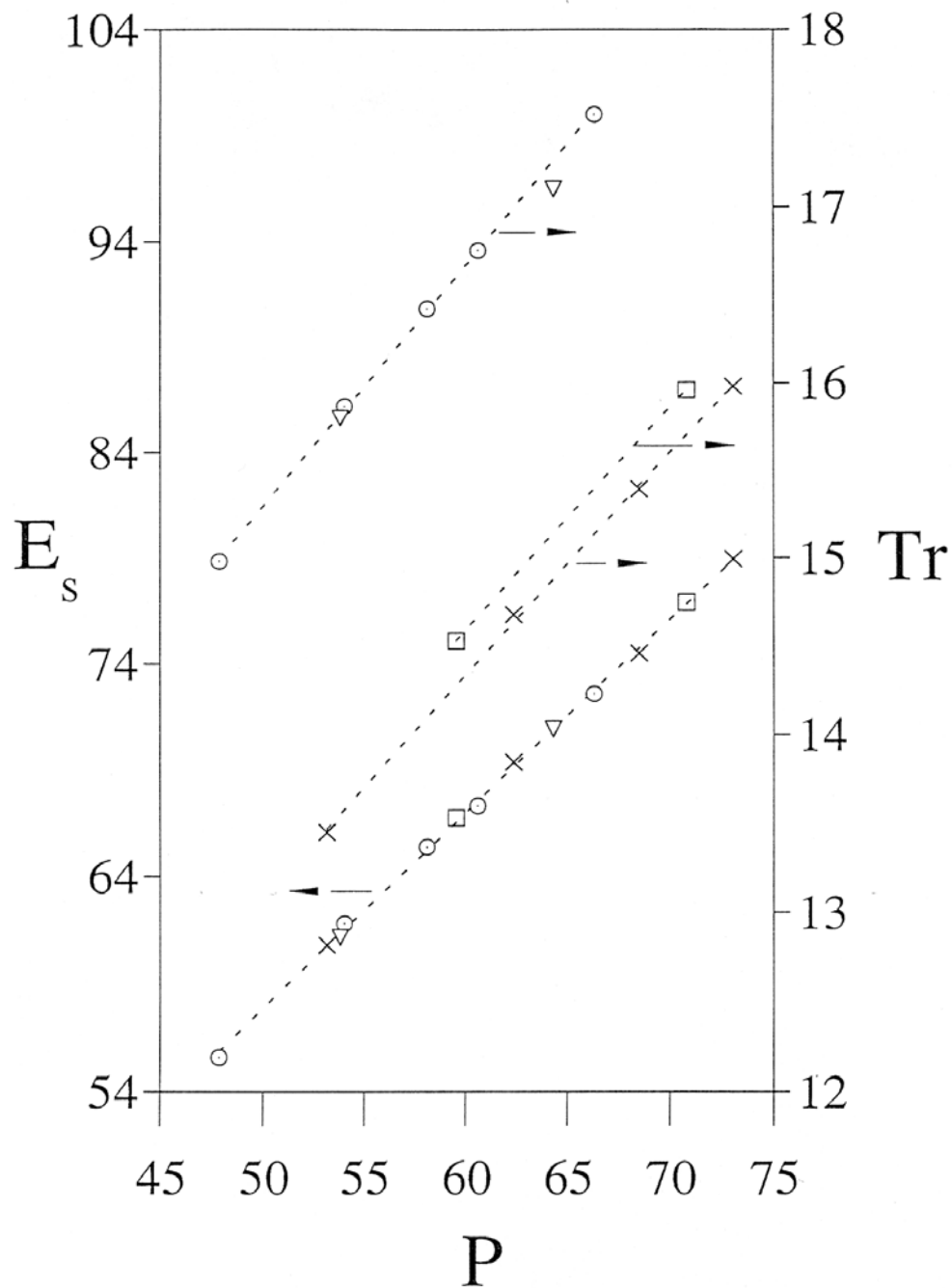
FIGURES



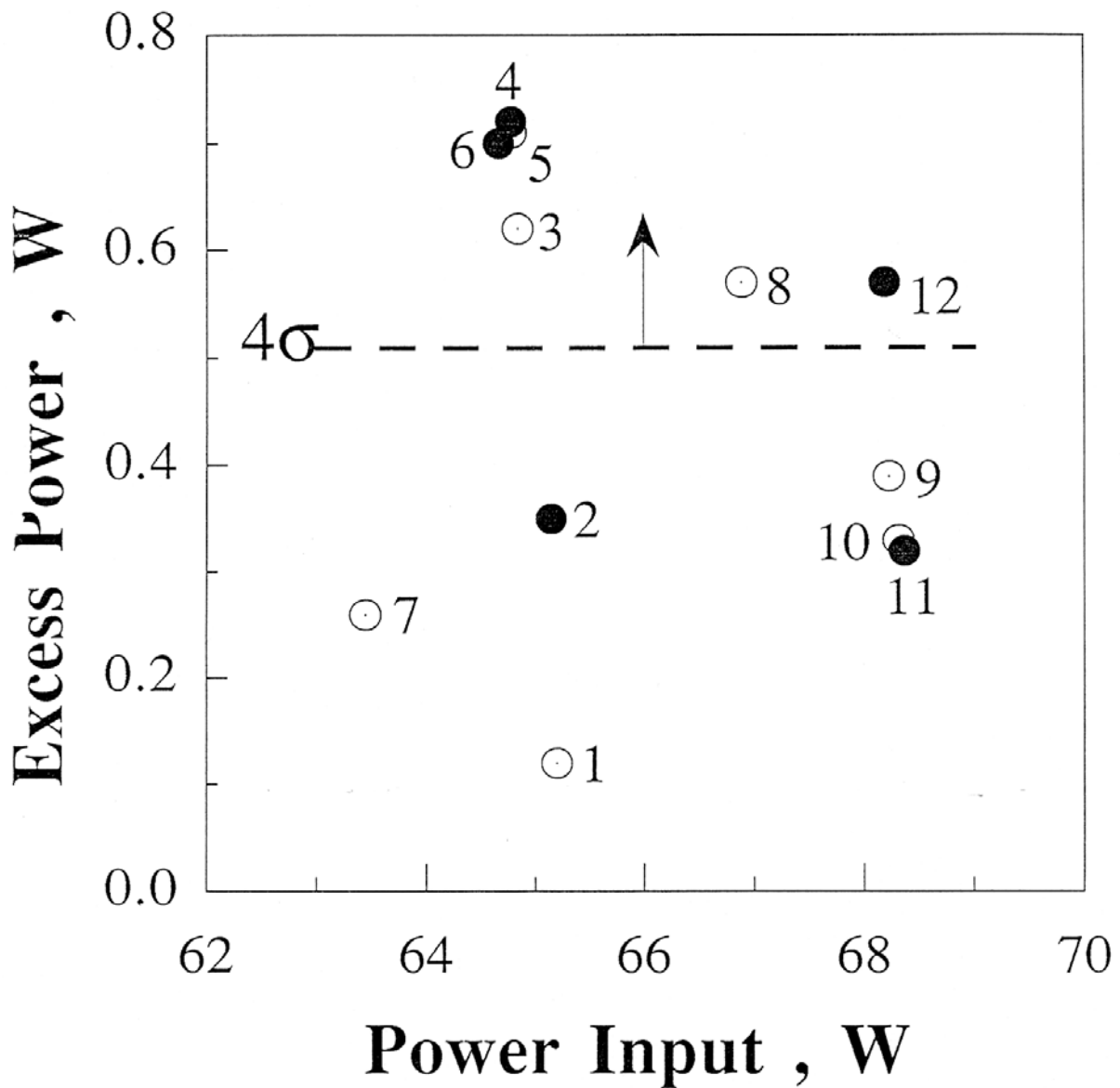
1. Schematic cross-sectional diagram of the Seebeck calorimeter. Supports and means of connections to specimen and to auxiliary heaters are not shown. Heating elements and multiple thermocouple sensors for the jacket are also not shown. A, sample; B, auxiliary heater; C, furnace; D, chromel-alumel thermocouple; E, reactor envelope; F, Seebeck box; G, copper enclosure; H, insulated jacket; I, vacuum and gas inlet tube; J, wire connections leading to instruments; K, insulating skirt.



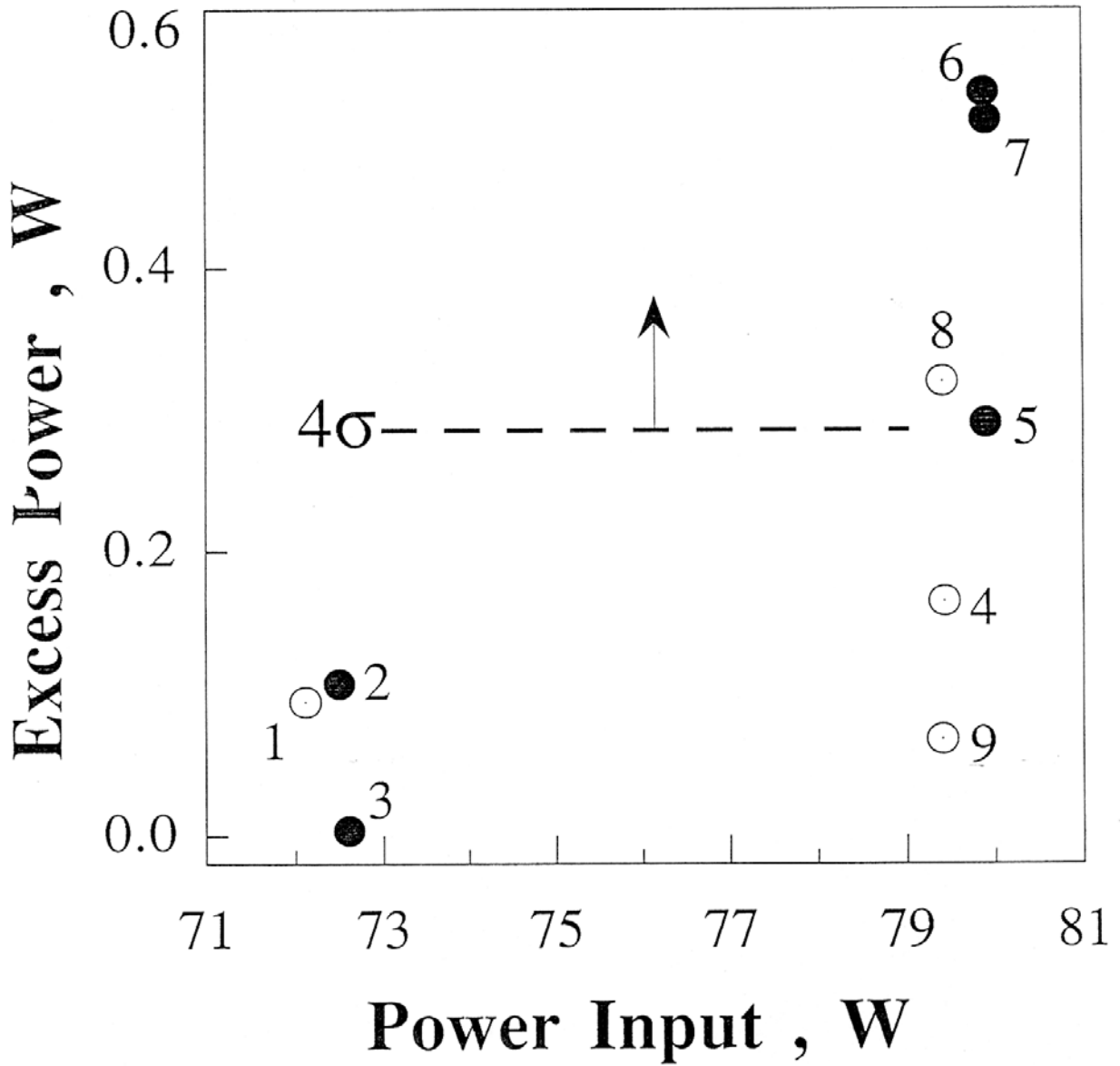
- Copy of chart of the strip chart recorder for a calibration run, showing stability of the signals.



3. Thermoelectric signal, E_s , of the Seebeck calorimeter vs. input electrical power, showing the absence of sensitivity to the nature of the gas phase. Contrastingly, the reactor temperature, T_R , measured by the internal chromel-alumel thermocouple is a strong function of the gas. (Circles) Argon at 1 atm; (X) helium at 0.4 atm; (Squares) deuterium at 0.2 atm; (Triangles) deuterium with a small amount of air.



- Excess power generated in experiment X. Calibration was done with D_2 and without a perovskite specimen in place. The specimen was subsequently installed in the reactor and operated under D_2 gas. Open circles represent episodes without d.c. power to the specimen and filled circles those with d.c. power. The numbers indicate the time sequence in which the data were measured. Points representing deviations larger than 4σ from the calibration lie above the dashed line.



5. Excess power generated in experiment B. Calibration was done with helium covering the specimen, after which the helium was replaced by deuterium. The data point symbols and numbers have the same significance as in Figure 4.