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ANALYSIS OF THE APPLICATION OF
THERMOGALVANIC CELLS TO THE
CONVERSION OF LOW GRADE HEAT
TO ELECTRICITY

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NOTICE

ANALYSIS OF THE APPLICATION OF THERMO-
GALVANIC CELLS TO THE CONVERSION
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Abstract

Aqueous thermogalvanic cells, the solution analogs of solid-state thermoelectric devices, are compared for power generation. Measurements on the copper|copper formate|copper system yield thermoelectric powers,$(\Delta E/\Delta T)_{I=0}$, of 1.25 - 1.9 mV/degree, which are higher than those exhibited by other copper systems. In these solutions three copper formate complexes are present. Practical cells were built and tested. The power output is largely limited by cell resistance, though mass and charge transfer contribute to the observed overvoltages. The coupling of this thermogalvanic system with an electrochemical photovoltaic effect (a photothermogalvanic cell) is briefly described.

Nomenclature

EMF	electromotive force
$(dE/dT)_{I=0}$	thermoelectric power, Seebeck coefficient
S_X	molal entropy of X
$\overline{S}_X$	partial molar entropy of X
S^*_X	entropy of transfer of X
$\overline{S}^*_X = \overline{S} + S^*$	total transported entropy
t	transference number
Z	figure of merit
n	efficiency
β_n	stability constant
ΔT	temperature differential
R	resistance of the solution

Background

Thermogalvanic Cells

Thermogalvanic cells can be defined as galvanic cells in which the temperature is not uniform. They are the electrochemical equivalent of thermoelectric devices, which convert heat into electricity. In these cells two or more electrodes are at different temperatures. These electrodes, not necessarily chemically identical or reversible, are in contact with an electrolyte, solid or liquid, not necessarily homogeneous in composition, and with or without permeable membranes interposed in the electrolyte. During the passage of current through the thermogalvanic cells, matter is transferred from one electrode to the other as a result of the electrochemical reactions at the electrode/electrolyte interface and ionic transport in the electrolyte. In this respect, the thermogalvanic cell differs from metallic thermocouples, or thermoelectric devices in general, in which no net transfer of material occurs, and the state of the conductor remains unchanged with the passage of current. In fact, thermoelectric effects in the metallic leads from the electrodes in the thermogalvanic cells contribute to the observed EMF of these cells.[1-5]

The EMF of a thermogalvanic cell in its initial state arises from three factors: (1) the differences in electrode temperature; (2) the thermal liquid junction potential; and (3) the metallic thermocouple effect. In general, the EMF arising from (1) and (2) is about two orders of magnitude larger than the EMF from (3), which arises at the junction in the external circuit between two electrode metals at different temperatures (the Seebeck effect). With the passage of time, a thermal cell is subject to thermal diffusion in the electrolyte (Soret effect), which tends to concentrate the more concentrated electrolytes in the cold region. The concentration gradient further changes the two electrode potentials, and the cell reaches a new stationary state (final EMF).[1-5]

The thermogalvanic cell can be written as $M(T_1)|electrode(T_1)|Electrolyte(T_1)|Electrolyte(T_2)|electrode(T_2)|M(T_1)$ where $T_2>T_1$. The electrodes can be metals or gases with inert electrodes.[1,2] The electrolyte can be a solution, a fused salt, or a solid electrolyte. Temperature T_1 is fixed and T_2 is varied. The most widely used sign convention for thermogalvanic cells is that the EMF(E) is positive when the terminal connected to the electrode at T_2 is positive with respect to that connected to the cold electrode. Therefore the hot electrode is the cathode, and the $(dE/dT_2)_{T_1}$ constant is positive. This coefficient $(dE/dT)_{thermal}$ is the thermoelectric power, sometimes also designated the "Seebeck coefficient" in analogy with the nomenclature used in thermoelectric phenomena.[6] The thermoelectric power is obtained from measurements at open circuit (I=0).

The thermoelectric power can be described as the sum of a heterogeneous term (due to the electrode temperature effect) and a homogeneous part (thermal liquid junction potential for solutions or the thermoelectric effect on solid or liquid

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ionic conductors). The driving force for the thermogalvanic cell is the transport of entropy from the high temperature reservoir (at T_2) to the low temperature sink (at T_1), as is the case in any heat engine.[1-5]

For a thermogalvanic cell, for instance, with pure metal electrodes and a simple electrolyte MX_n, solid or fused, the EMF of the cell is the electrical potential of a wire attached to the hot electrode minus the potential of a similar wire attached to the cold electrode. The electrical work for n equivalents of electricity is determined by the entropy absorbed from the heat reservoir surrounding the hot electrode when positive electricity passes through the cell from the cold to the hot electrode.[7] This entropy is identical to the sum of the entropy absorbed in the electrode reaction, [in this case, S_M(molal entropy of the metal)-$\bar{S}_{M^{n+}}$(partial molar entropy of M^{n+})-$n\bar{S}_{e(M)}$(partial molal entropy of the electron in M)] and the entropy transported away from the hot electrode [in this case, $-\bar{S}^*_{M^{n+}}$(entropy of transfer of M^{n+})-$nS^*_{e(M)}$(entropy of transfer of e^-)].[3-7] The entropies of transfer result from heat effects attributable to the movement of electrons and ions through a thermal gradient under the influence of a voltage drop. Since $\bar{S} + S^* = \bar{S}$ (total transported entropy), one can write:

$$nF \frac{dE}{dT} = S_M - \bar{S}_{M^{n+}} - n\bar{S}_{e^-(M)} \tag{1}$$

This expression also holds for aqueous thermocells[1] after the Soret equilibrium is reached (final EMF). For the initial EMF of such aqueous thermocells (uniform electrolyte distribution) the term $t_-(S^*_{M^{n+}} + nS^*_-)$, where t_- is the transference number of the anion, must be added to that expression.

The thermoelectric power, $(dE/dT)_{thermal}$ measured at I=0 or calculated from the appropriate equation has been used to calculate the figure of merit, Z, of the thermogalvanic cell,[5] in analogy to that used for thermoelectric devices[6]

$$Z = \frac{(dE/dT)^2_{I=0}}{\rho\kappa} \quad \text{in } K^{-1} \tag{2}$$

where ρ = specific resistivity in ohm-cm, κ is the specific thermal conductivity in $Wcm^{-1}K^{-1}$, and dE/dT is in VK^{-1}. Ionic conductors were found to have figures of merit of approximately $10^{-3}K^{-1}$, which are of the order of magnitude of the thermoelectric semiconducting devices.[6] The conversion efficiencies are Carnot cycle limited for both the thermoelectric and thermogalvanic cells. However, anticipated practical figures of merit would be consistently less than those obtained from I=0.

The expression of Telkes[8] for solid state device efficiencies, η, has been applied to thermogalvanic cells:

$$\eta = \frac{1}{\frac{2 T_2}{T_2-T_1} + \frac{4\kappa\rho}{\left(\frac{dE}{dT}\right)^2_{I=0} (T_2-T_1)}} \times 100\% \tag{3}$$

where the first term in the denominator is related to the Carnot efficiency and the second is related to the figure of merit. Other expressions have been calculated for molten salt thermogalvanic cells.[9]

The analyses of Z and η above do not consider electrode polarization effects which effectively limit the power output of such devices under current drain.

Some thermogalvanic cells have been investigated for power generation.[10] Molten salts[11] and solid electrolytes[12] were chosen for these devices. In these media wide operating temperature ranges are possible, and therefore, large Carnot efficiencies.

In this paper we are interested in the conversion of low grade heat into electricity. Examples of sources of free low grade heat are OTEC (Ocean Thermal Energy Conversion), geothermal, waste industrial heat, etc.. Solar ponds are also a source of low grade heat. In this context the range of 20 - 80°C is of importance. Aqueous electrolytes are suitable for this temperature range. This paper reviews three types of thermogalvnic cells in aqueous media and presents new data on a copper system. A preliminary analysis of the suitability of such systems for power generation utilizing a low grade heat source will be presented at the meeting.

Aqueous Thermogalvanic Cells

Three general types of thermogalvanic cells can be singled out:

(1) Metal electrodes immersed in unsaturated solutions of salts, therefore two electrodes of the first kind (M/M^{n+}):

$$M(T_1) \mid MA \mid M(T_2).$$

Cells of this type have long been studied.[1,2] An example is $Cu|CuSO_4$ unsaturated|Cu.

(2) Metal electrodes immersed in saturated solutions of salts, separated by a salt bridge:

$$M(T_1) \mid MA(T_1, a_1) \mid\mid MA(T_2, a_2) \mid M(T_2).$$
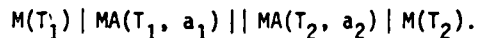
Clampitt and German[13] patented and measured some of these cells, e.g., $Cu|CuSO_4$ satd. $T_1 \mid\mid CuSO_4$ satd. $T_2|Cu$ in aqueous, aqueous acid, and non-aqueous media.

(3) Redox soluble couples with inert electrodes (E):

$$E(T_1) \mid M^{m+}, M^{n+} \mid E(T_2),$$
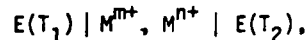
suggested by Burrows,[14] and measured for the $Pt|Fe^{3+}, Fe^{2+}|Pt$ and $Pt|Fe(CN)_6^{4-}, Fe(CN)_6^{3-}|Pt$ systems.

In the first two types of thermogalvanic cells described above, the electrodes undergo permanent changes, with anodic dissolution at one temperature, and cathodic deposition at the other. In order to

continuously produce electricity from these cells, the temperature of the electrodes has to be reversed periodically. In the second type, couples are chosen such that the solubility of MA varies widely with temperature. The activity of M^{n+} ions in each chamber is kept reasonably constant under current drain, by the precipitation or dissolution of MA, coupled to the electrode processes. There is anion transfer from one to the other side of the cell. In the third type, since the redox couple is soluble, there are no permanent changes at the electrodes, and the devices can be operated continuously provided there is a temperature differential.

The first two types can present dendrite growth at the metal electrode/electrolyte interface, which can create practical difficulties such as short circuits. All of these cells can present activation (charge transfer) and/or concentration (mass transfer) polarization in addition to ohmic polarization, which decrease the power output. For type (2) the dissolution and/or precipitation of MA can be rate limiting.

Table I compares the thermoelectric powers for examples of these three types of cells, and, when available, the power output of these systems.

TABLE I - THERMOELECTRIC POWERS FOR SOME SELECTED
THERMOGALVANIC CELLS IN AQUEOUS MEDIA

System	$(dE/dT)_{I=0}$ (mV/degree)	Temperature (°C)		Power Output ($\mu W/cm^2$)	Reference
Cu|electrolyte|Cu					
Electrolyte (unsaturated)					
$[CuSO_4]$ 0.08 M	0.64			-	1
0.5 M	0.73	0-50°C		-	1
1.0 M	0.69-0.79			-	1
satd.	0.9-0.97			-	1
		t_{cold}	t_{hot}		
0.01 M; pH = 4.65	1.0	25	75	-	15
0.01 M; pH = 1.8-1.0	0.5-0.3	25	85	-	15
NaCl					
15% w/w	-0.35	19	100	-	16
5% w/w	-0.24	19	100	-	16
Electrolyte (saturated)					
saturated in H_2O	0.89	20	100	30.5	13
saturated in 20% H_2SO_4	1.03	20	100	251(?)	13
Redox Thermogalvanic					
$Pt\|Fe^{2+}, Fe^{3+}$; 1 M HCl|Pt					
$[Fe^{2+}]=[Fe^{3+}]$ = 2 M	0.57	30	80	<42*	14a
1 M	0.78	30	80	<25*	14a
0.25 M	1.0	30	80	<13*	14a
$Pt\|Fe(CN)_6^{4-},Fe(CN)_6^{3-}$ 0.5M K_2SO_4|Pt $[Fe(CN)_6^{4-}]=[Fe(CN)_6^{3-}]=$					
0.2 M	-	30	80	<90*	14b
0.1 M	1.44	30	80	<50*	14b
0.05 M	-	30	80	<30*	14b

*Maximum power, IR free values.

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For type (3) the coupling of the thermogalvanic cell with an electrochemical photovoltaic effect was proposed by Burrows[14] for the cell (hot)n-TiO$_2$|Fe(CN)$_6^{4-}$,|Fe(CN)$_6^{3-}$|Pt(cold). Such cell was called photothermogalvanic. No data have been published to date.

In 1917, Case[17] described that copper electrodes immersed in copper formate solutions, within a certain range of acidity, displayed an electrochemical photovoltaic effect, when the anode was illuminated and the cathode kept in the dark. Alternating current was produced by reversing the illumination process, i.e., by illuminating the previously dark cathode, now anode, and keeping the other electrode in the dark. Jayadev[18] confirmed Case's results on the observed photoeffect. In this paper we report the preliminary results on the investigation of the copper-copper formate thermogalvanic system. The initial results on the coupling of the thermogalvanic cell with the electrochemical photovoltaic effect, to be called photothermogalvanic effect, are also reported.

II. Experimental Part

The discharge behavior of the thermogalvanic cells was investigated in U-shaped cells with jacketed arms, similar to that described in reference 14. The temperature in each half cell was controlled to ±0.2°C by a continuous flow of water from two thermostated water circulators (Lauda Brinkman K/2R and Haake F-3). Cold electrode temperatures were maintained at 10 to 20°C and the hot half-cell temperature was varied between 30 and 80°C.

Copper electrodes were made of pure copper sheets (99.9995%, Electronic Space Products, Inc.), spot welded to copper wires. The wire and the back of the electrodes were coated with Miccroflex (Miccro product) paint, resistant to the investigated solutions under the experimental conditions. Copper reference electrodes were also made of copper wires (99.9995, Electronic Space Products Inc.) protected from contact with the solution by the Miccroflex paint with the exception of the last 0.3 cm.

A sample of copper formate (Cu(HCOO)$_2$·4 H$_2$O, 98%) was provided by Kocide Chemical Corporation. Reagent grade sodium formate (Baker), formic acid (Baker), copper sulfate pentahydrate (Mallincrodt), sodium tetrafluoroborate (Alfa), sulfuric and nitric acids (Baker) were employed. Solutions of copper salts were made up with deionized water which was previously boiled and rapidly cooled down. A plastic glove bag (I^{2}R) under nitrogen was used for the preparation and transference of solutions. The pH of the solutions was measured with a Beckman digital pH meter no. 3560 and with Orion combination electrodes (91-02).

A potentiostat-galvanostat, Princeton Applied Research Corporation (PARC) 173 D with 176 current voltage converter or 376 digital coulometer was employed as a source of constant current or potential. The digital voltmeter Keithley model 174 was employed. A conductivity bridge (Sybron-Barnstead, PM-70CB) was used for room temperature measurements. A current-interruptor technique was employed for the measurement of the resistance of

the solutions in the thermogalvanic cells.

The more practical cells tested were made of PVC tubing (2.5 cm diameter) and variable length (1.25 to 5.0 cm). Copper electrodes were attached to the PVC with the Miccroflex paint. In these cells the temperature at each electrode was maintained through a copper heat-exchanger with a copper plate (7 cm diameter) which was soldered to copper tubing in the back. Water from the thermostated circulators flowed through the tubing.

Temperatures were measured with a Bailey Instruments digital thermometer BAT-9 with microprobes (ICT-4) or copper-constantan thermocouples.

A slide projector with a tungsten light source (300 W bulb) was used for illuminating the electrodes in the U shaped cells. Filters were employed and the intensity of the radiation was measured with a thermopile (The Eppley Laboratory, Inc.).

III. Results and Discussion

The thermogalvanic cell Cu|copper formate|Cu has a positive hot electrode (cathode) and positive values of the thermoelectric power $(\Delta E/\Delta T)_{I=0}$. From data obtained in U tube cells, the thermoelectric power of this system was measured as a function of copper formate concentration, free formate concentration, free formic acid concentration, pH, and temperature range ($\Delta T = 20 - 70$°C), as well as the discharge characterisitcs of these cells. In going from 0.11 M concentration of Cu(HCO$_2$)$_2$·4H$_2$O to 0.35 M, the thermoelectric power increases from 0.62 to 1.25 mV/degree, for an added formic acid concentration of 0.16 M, and a $\Delta T = 45$°C.

The species distribution in copper formate solutions was determined by Tedesco and Quintana[19], in ionic strength 1, perchloric medium, formic acid concentration 0 - 0.7 M, using potentiometric and polarographic methods. The formation constants are: β_1(Cu(HCO$_2$)$^+$) = 14; β_2 (Cu(HCO$_2$)$_2$) = 30; and β_3 (Cu(HCO$_2$)$_3^-$) = 82. Spectrophotometric data[20] at 25°C, in a medium of ionic strength of 3 (adjusted with KNO$_3$), and constant free formic acid concentration of 0.1 M are: β_1(Cu(HCO$_2$)$^+$) = 50, β_2 (Cu(HCO$_2$)$_2$) = 102, and β_3 (Cu(HCO$_2$)$_3^-$) = 192. No data are available at higher temperatures. The differences in the conditions employed and methods, justify the differences in equilibrium constants. Utilizing the data above[19], the copper formate solutions above contain at 25°C, all three copper formate complexes and a smaller amount of the aquo-complex. Increased total formate concentration, as sodium formate, favors the formation of Cu(HCO$_2$)$_3^-$ (30, 50 and 65% respectively in going from 0.44 to 0.88 to 1.18 M added NaHCO$_2$, to a 0.35 M Cu(HCO$_2$)$_2$·4H$_2$O solution, and the pH increases from 3.90 to 4.23 to 4.35). Under those conditions the thermoelectric power decreases slightly: 1.25 to 1.20 to 1.00 mV/degree ($\Delta T = 45$°C). At higher temperatures it is likely that the formate complex species will undergo dissociation, and that aquo-copper complexes are present to a larger extent.

The thermoelectric power appears to be a function of the free formic acid concentration. For solutions containing 0.35 M Cu(HCO$_2$)$_2$·4H$_2$O, and ~0.35 M NaHCO$_2$, (and approximately the same distri-

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bution of copper species and free formate) the thermoelectric power increases from 1.25 to 1.65 mV/degree ($\Delta T = 45^{\circ}C$) as the free formic acid concentration decreases from 0.50 to 0.30 M. The thermoelectric power generally increases with increased ΔT. For instance, for the solution above with free formic concentration of 0.50 M the thermoelectric power increases from 1.48 to 1.58 to 1.79 to 1.86 mV/degree for ΔT of 30, 40, 50 and 60°C respectively.

The concentration of copper formate of 0.35 M was chosen as upper concentration limit for being close, but less than the solubility at the low temperature half cell (10 - 20°C).

The data above were obtained by cleaning the electrodes in 10-20% v/v HNO_3, followed or not by mechanical polishing, and letting the electrodes stand in solution for at least 2-3 hours in the dark. Current-voltage curves were obtained. Reference electrodes at each half-cell indicated that the overvoltages are generally higher at the lower temperature electrode. Both mass transfer and charge transfer seem to contribute to the observed overvoltages. These are, however, smaller than the ohmic overvoltage. The current-voltage curves were reproducible. For instance, for a 0.35 M $Cu(HCO_2)_2 \cdot 4H_2O$, 0.35 M $NaHCO_2$, and added formic acid of 0.08 M, the product V open circuit (V_{OC}) times I short circuit (I_{SC}), $V_{OC} \times I_{SC} = 54.9 \times .181 = 9.94$ μW was obtained, and after a week, $V_{OC} \times I_{SC} = 53.3 \times .185 = 9.86$ μW, for a $\Delta T = 35^{\circ}C$

Addition of sodium salts, e.g., sodium tetrafluoroborate, decreases slightly the thermoelectric powers, and the power output of the systems. The resistance of the solution decreases as expected. The investigated concentration range of $NaBF_4$ was 0.35 to 1.0 M.
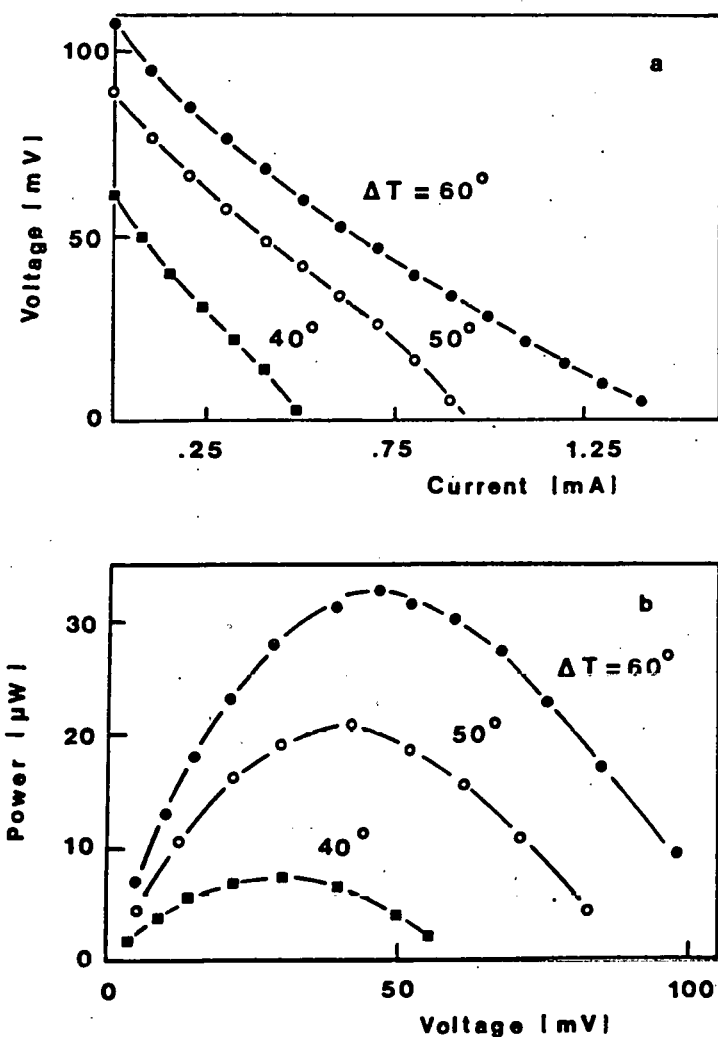

Figure 1. (a) Voltage-current characteristics of the copper|copper formate|copper thermogalvanic cell as a function of the temperature differential. Electrode area: 4.5 cm²; Cell length = 5.0 cm. (b) Power output vs. voltage of the copper|copper formate|copper thermogalvanic cell. Total copper concentration: 1.13 M; pH = 3.6 (20°C). Only representative points shown.

A more practical cell was built with a PVC tube (2.5 cm diameter), 5 cm length, and filled up with a solution 0.35 M $Cu(HCO_2)_2 \cdot 4H_2O$, 0.35 M $NaHCO_2$, and 0.08 M added formic acid. The area of the copper electrodes was 4.5 ± 0.5 cm^2. The above Figure 1a shows the voltage-current characteristics of this cell for three temperature differentials. From the curves in Figure 1a, one can conclude that charge and mass transfer are important in this system, in addition to ohmic activation, responsible for the major power losses (R (ΔT =0) $\sim$ 90 ohms). The resistance decreases with increased ΔT (ΔT = 60°C, R $\sim$60 ohms). These cells are very inexpensive. $0.15 is the cost of the chemicals, except for the copper electrodes, which determine the overall cost of the cell. These aqueous cells are much less expensive than the equivalent solid state thermoelectric devices to date. Estimated maximum power density for ΔT = 60°C is about $20\mu W/cm^2$. The above Figure 1b illustrates the power outputs of the cell as a function of the voltage.

Smaller cells (2.5 and 1.25 cm length) were also built and tested in a variety of solutions. For copper formate solutions containing 1 M $NaBF_4$, at ΔT = 40°C, 2.5 cm cells gave a maximum power of 11.8 μW (electrodes of 1-1.5 cm^2 area). Halving the length the power output of 10 μW was obtained, suggesting that for these solutions the temperature gradients may not have been maintained. For ΔT = 50°C, cells 1.25 cm long gave 9.5 μW with 0.35 M $NaBF_4$. By comparison, the same cell filled with $CuSO_4$(0.35 M) gave 3.3 μW (ΔT = 50°C), whereas twice the length gave 5.8 μW. The addition of sulfuric acid (20% v/v) increased the power by a factor of 2. The optimum length for these systems is between 2.5 and 5 cm.

These cells are being employed to investigate comparatively the power outputs of the thermogalvanic cells types (1) to (3). Type (3) is being investigated on graphite electrodes. The efficiency of these devices under load is being measured. These data will allow us to analyze the feasibility of the coupling of these inexpensive devices to convert free low grade heat into electricity.

Case[19] suggested that copper electrodes in copper formate solutions form a layer of Cu_2O, the semiconductor electrode. This red layer is formed upon standing or by potentiostatic or galvanostatic methods. A solution 0.35 M in $Cu(HCO_2)_2 \cdot 4H_2O$, 0.35 M in $NaHCO_2$, and approximately 0.2 M in added formic acid was placed in the U tube cell, with a ΔT = 30°C. The copper electrodes were plates 4 x 0.5 x 0.1 cm., immersed in the solution for 2 days, after which a red uniform coating of Cu_2O was formed. Figure 2 shows a comparison of the voltage current curves for a ΔT = 30°C in the dark, and upon illumination[b] (45 $\mu W/cm^2$) of one of the faces of the anode (the cold electrode). Upon illumination a photovoltage is added to the thermovoltage. The photovoltage slowly but continuously decays. The power output upon illumination practically doubles. The photoeffect observed is an electrochemical photovoltaic effect, since it is not present when pure copper electrodes are illuminated. In order to restore light sensitivity of the illuminated electrode, it has to be reduced in the dark. This effect is being investigated. Surface analyses are being employed to characterize the

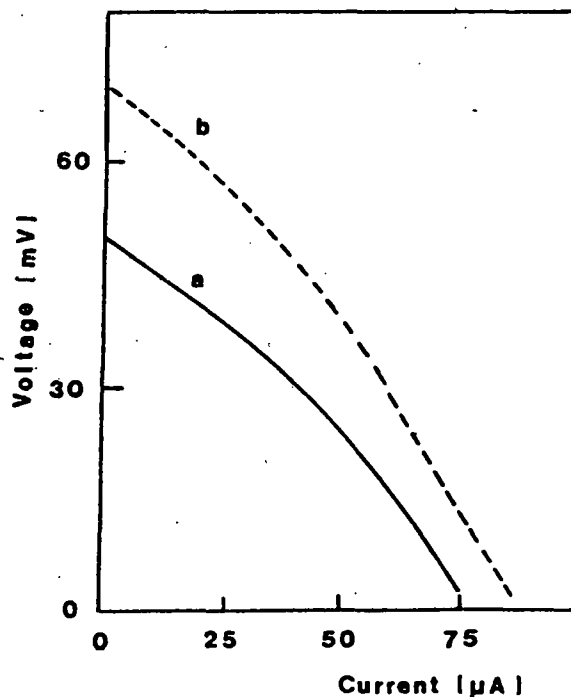nature of the electrodes in the dark and after illumination in these cells.

FIGURE 2. Voltage-current characterisitics of the copper|copper formate|copper thermogalvanic cell (a) in the dark; (b) with the cold anode illuminated at 45 $\mu W/cm^2$. Total copper concentration: 0.35 M; total formate concentration: 1.25; pH: 3.7(20°C). Only representative points shown.

IV. Conclusion

The copper|copper formate|copper system was investigated. Practical thermoelectric powers, $(\Delta E/\Delta T)_{I=0}$ of 1.25 to 1.9 mV/degree can be obtained in this system, depending on the copper formate, free formic acid concentration, as well as on the temperature difference between the cold and hot half-cells. These powers are higher than those obtained in other copper salt systems, and in other systems as well (see Table I).

Current-voltage curves indicate that in addition to ohmic drop, activation and concentration overpotentials limit the power output of these devices.

Practical cells were built and maximum power outputs of about 20 $\mu W/cm^2$ estimated.

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The coupling of the thermogalvanic with an electrochemical photovoltaic effect, the photo-thermogalvanic cell, was shown for the first time in this system.

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