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**Comments and Addenda**


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**Comments on "Power conversion of energy fluctuations"**

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(Received 10 January 1978)

The equations used by Yater to calculate dc power conversion of energy fluctuations are shown to contain mistakes which prohibit their use in general calculations. Corrected equations are presented which converge to known results in the limit of large capacitances: Yater's conversion-efficiency equations do not. Calculations with the present equations are used to demonstrate that the high conversion efficiencies approaching the Carnot cycle do occur, but only for circuit situations where the power output is considerably below the maximum obtainable fluctuation power and where the circuit capacitances are impractically small ( $\approx 3 \times 10^{-19}$  F). Conversion efficiencies at the maximum output power are considerably smaller than the Carnot-cycle limit. No net power conversion is predicted for practical circuit capacitances.

**INTRODUCTION**

Yater<sup>1</sup> proposed that rectification of fluctuation voltages could provide high-efficiency power conversion from thermal energy to dc electrical power. Predicted efficiencies approached the Carnot cycle limit. These results have stimulated broad interest in the concept. However, his equations contain errors that require correction before the concept can be studied for a wide variety of circumstances. Also, the presentation of the results was in a normalized form so that the practicality of the concept cannot be readily evaluated.

It is the intent here to correct the equations and use the corrected equations to calculate thermal-to-dc power-conversion efficiency in an unnormalized fashion. Extensive calculations are carried out and presented. The results show that the errors in Yater's equations are circumvented for the limited situation he calculated, namely, matched diodes where the differences in work functions buck each other in his equations. It is found that there are situations where conversion efficiencies approach the Carnot cycle limit, but only when total circuit capacitances are impractically small and when circuit impedance mismatches are so great that the available output power is considerably below the available fluctuation power. Conversion efficiencies for situa-

tions where the maximum power output is obtained are less than half the Carnot cycle limit.

**THEORY**

The general philosophy used here and by Yater<sup>1</sup> is a statistical-mechanical formulation of nonlinear circuits where noise voltage and current fluctuations are an appreciable fraction of the circuit voltages and currents. Intuitively, this situation should arise only when circuit capacitances are small so that small numbers of electrons can influence circuit voltages. The formulation chosen is the "master equation" approach of Van Kampen.<sup>2</sup>

The circuit analyzed by Yater uses diodes as the nonlinear elements and is given in Fig. 1. The left-hand side of Fig. 1 is at a high temperature  $T_h$  relative to the right-hand side  $T_c$ . The components  $A$  and  $G$  are the saturation currents flowing from the high-work-function sides of the diodes while  $B$  and  $D$  are the components flowing from the low-work-function sides. The capacitances  $C_c$  and  $C_r$  represent the capacitances of the respective diodes plus any stray shunt capacitances. The diodes in Fig. 1 will be fashioned after the so-called Alkemade<sup>3</sup> diode (considered by Van Kampen<sup>2</sup>), which is an isolated diode without consideration of external circuitry. Yater<sup>1</sup> used Van Kampen's equations with external circuitry,

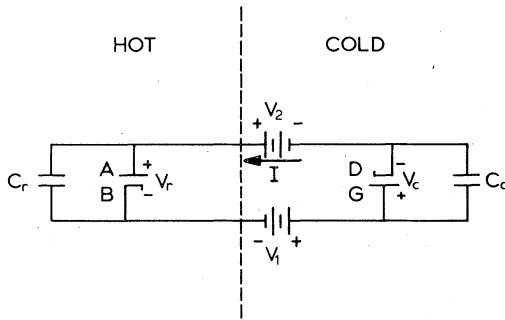


FIG. 1. Circuit analyzed in Ref. 1 and in the present work. The hot side  $T_r$  and cold side  $T_c$  are assumed to be thermally isolated so only electrical power flows in the circuit.  $A$ ,  $B$ ,  $D$ , and  $G$  are individual currents in the diodes.

and his resulting set of equations mix diode-work-function differences and circuit voltages together in circuit equations, a situation which is physically unrealistic and which occurs whenever Fermi levels are not properly matched when formulating an energy-level diagram for the circuit. It will be necessary to emphasize this aspect with some tedious detail on diode equations.

Consider the left-hand diode in Fig. 1. The saturation electrical current  $A$  for the high-work-function side of our diodes will be given by

$$A = 4\pi qm(kT_r)^2 h^{-3} O \exp(-W_A/kT_r), \quad (1)$$

where  $m$  is the electron effective mass,  $k$  is Boltzmann's constant,  $T_r$  is the absolute temperature,  $h$  is Planck's constant,  $q$  is the electronic charge,  $O$  is the diode area,  $W_A$  is the work function of the material, and current is defined as the flow of positive charge. The electrons on the low-work-function side see a potential barrier  $\phi$  given by

$$\phi = W_A - W_B - qV_r, \quad (2)$$

where  $W_B$  is the work function for side  $B$  and  $V_r$  is the potential across the diode, as in Fig. 1. This potential barrier is the proper potential barrier to use for a diode when the Fermi levels in  $A$  and  $B$  are matched at thermal equilibrium. The current component  $B$  is the saturation current times the Boltzmann factor for that barrier:

$$B = 4\pi qm(kT_r)^2 h^{-3} \times \exp[-W_B/kT_r - (W_A - W_B - qV_r)/kT_r], \quad (3)$$

where  $m$  is taken to be the same as for the  $A$  side. The result is standard:

$$B = A \exp(qV_r/kT_r). \quad (4)$$

Identical equations can be derived for  $G$  and  $D$ ,

the result being

$$D = G \exp(qV_c/kT_c). \quad (5)$$

Consider a noise-free circuit first. A dc current  $I$  flows in the direction indicated and is given by either

$$I = A[\exp(qV_r/kT_r) - 1] \quad (6)$$

or

$$I = G[\exp(qV_c/kT_c) - 1] \quad (7)$$

because of current continuity conditions.

The Kirchhoff law gives

$$V_1 + V_2 = V_c + V_r, \quad (8)$$

where  $V_1$  and  $V_2$  are the battery voltages in Fig. 1. Equations (6) and (7) can be equated and Eq. (8) used to eliminate either  $V_c$  or  $V_r$ ; the result is a transcendental equation in the remaining diode voltage. These noise-free solutions will be used here extensively. Yater solved the noise-free dc situation assuming that the battery voltages divide across  $C_c$  and  $C_r$  as though  $C_c$  and  $C_r$  were in series with no shunt paths; this error will have serious consequences, as shown later. In reality these voltages divide according to the shunt paths described by the diode equations 6-8.

The noise fluctuations in the circuit will be treated following Van Kampen and Yater. Consider state  $N$ , the condition when there are  $N$  electrons on the upper half of the circuit in Fig. 1 which are in excess of the steady-state, or equilibrium, value defined by Eqs. (6)-(8). The change in energy across the combined capacitance  $C$ ,

$$C = C_c + C_r, \quad (9)$$

to go from state  $N$  to state  $N+1$  is

$$q^2(N+1)^2/2C - q^2N^2/2C = q^2(N + \frac{1}{2})/C. \quad (10)$$

This voltage fluctuation appears across the diodes and is opposite in sign for the two diodes. The current flowing while the circuit is in state  $N$  will differ from Eqs. (6) and (7) because the barriers for both diodes are modified by the expression in Eq. (10). Thus the electrons on the low-work-function side see a fluctuating barrier and a fluctuation current flows. Our task is to determine the rectified portion of that fluctuation current because it represents the power conversion of thermal energy from the hot side.

The master equation developed by Van Kampen is derived by writing the rate of change of probability  $P(N)$  of being in the  $N$  state. The current components  $A$ ,  $B$ ,  $D$ , and  $G$  represent the time-average flow of current across the diodes and are the mechanism by which the circuit transits

between states. We find that

$$\begin{aligned} \frac{q}{dt} \frac{dP(N)}{dt} = & AP(N+1) - AP(N) + AP(N-1) \exp\left\{\frac{qV_r - q^2(N - \frac{1}{2})/C}{kT_r}\right\} - AP(N) \exp\left\{\frac{qV_r - q^2(N + \frac{1}{2})/C}{kT_r}\right\} \\ & + GP(N-1) - GP(N) + GP(N+1) \exp\left\{\frac{qV_c + q^2(N + \frac{1}{2})/C}{kT_c}\right\} - GP(N) \exp\left\{\frac{qV_c + q^2(N - \frac{1}{2})/C}{kT_c}\right\}. \end{aligned} \quad (11)$$

This master equation is almost identical to that of Yater except that the work function differences are not mixed with  $V_c$  and  $V_r$ , because they are accounted for by the choice of energy barrier in Eq. (2), and  $V_c$  and  $V_r$  are determined correctly

by Eqs. (6)–(8) instead of by capacitance ratios. If the operator  $F$  is defined by

$$Ff(N) = f(N+1), \quad F^{-1}f(N) = f(N-1), \quad (12)$$

then Eq. (11) can be written

$$\frac{q}{G} \frac{dP(N)}{dt} = (F^{-1} - 1)(1 + K \exp\left\{\frac{qV_r - q^2(N + \frac{1}{2})/C}{kT_r}\right\})P(N) + (F - 1)(K + \exp\left\{\frac{qV_c + q^2(N - \frac{1}{2})/C}{kT_c}\right\})P(N), \quad (13)$$

where

$$K = A/G. \quad (14)$$

Equation (13) can be factored to obtain

$$\frac{q}{G} \frac{dP(N)}{dt} = (F - 1) \left[ (K + \exp\left\{\frac{qV_c + q^2(N - \frac{1}{2})/C}{kT_c}\right\})P(N) - (1 + K \exp\left\{\frac{qV_r - q^2(N - \frac{1}{2})/C}{kT_r}\right\})P(N-1) \right], \quad (15)$$

which leads for the equilibrium case to the recursion relation ( $P$  must vanish as  $N \rightarrow \infty$ ):

$$P(N) = \frac{1 + K \exp\left\{\frac{qV_r - q^2(N - \frac{1}{2})/C}{kT_r}\right\}}{K + \exp\left\{\frac{qV_c + q^2(N - \frac{1}{2})/C}{kT_c}\right\}} P(N-1). \quad (16)$$

This recursion relation is similar to that of Yater's Eq. (10) except that differences in work functions are not mixed with  $V_r$  and  $V_c$ , and  $V_r$  and  $V_c$  are determined by Eqs. (6)–(8). The recursion relation of Eq. (16) and the normalization condition

$$\sum_n P(N) = 1 \quad (17)$$

allow calculation of  $P(N)$  for given  $K$ ,  $V_1$ ,  $V_2$ ,  $T_r$ , and  $T_c$  values.

If  $V_1 = -V_2$  in Fig. 1, then Eqs. (6)–(8) tell us that  $V_r = V_c = 0$ . The resulting  $P(N)$  for  $T_c = T_r = T$  in Eq. (16) is

$$P(N) = \exp(-q^2 N^2 / 2kTC) P(0). \quad (18)$$

This Gaussian distribution symmetric about  $N = 0$  is obtained for any  $|V|$  and any two diodes as long

as  $V_1 = -V_2$  and  $T_r = T_c = T$  and is an expected result. However, this result occurs for Yater's equations only when  $|V_1|$  and  $|V_2|$  are chosen equal to the work-function differences of the diodes, and the polarities of the batteries are chosen to buck the differences in work functions of the diodes in his equations.

#### POWER CONVERSION

If the fluctuation voltages become large enough, i.e., if the circuit total capacitance becomes small enough, the nonlinearity of the diodes will cause rectification. We follow the procedure of Yater. The net current flow on the cold side taking the circuit back and forth between state  $N$  and state  $N-1$  is given by  $I(N)$  as

$$\begin{aligned} I(N) = & GP(N) \exp\left\{\frac{qV_c + q^2(N - \frac{1}{2})/C}{kT_c}\right\} \\ & - GP(N-1). \end{aligned} \quad (19)$$

This term summed over all  $N$  is the total dc current  $I_t$ . Equation (16) can be used to eliminate  $P(N-1)$  in Eq. (19):

$$I_t = \sum_N KGP(N) \frac{\exp[qV_c/kT_c + qV_r/kT_r + q^2(N - \frac{1}{2})(T_r - T_c)/kCT_r] - 1}{1 + K \exp[qV_r - q^2(N - \frac{1}{2})/C]/kT_r} \quad (20)$$

In the limit of large  $C$  where fluctuation voltages go to zero, Eq. (20) reduces with some algebra and the help of Eqs. (6), (7), and (17) to

$$\lim_{C \rightarrow \infty} (I_t) = G [\exp(qV_c/kT_c) - 1], \quad (21)$$

the expected macroscopic result.

The dc power output  $P_w$  is given by

$$P_w = I_t(V_1 + V_2). \quad (22)$$

This power input, as defined by Yater, is the net power dissipated on the cold side. He neglects conductive heat transfer from the hot side to the cold side; we do the same here for comparison purposes. The incremental instantaneous power dissipation on the cold side is defined as  $I(N)$  times the average voltage drop it flows through during the transition from state  $N$  to state  $N - 1$ .

$$P_c(N) = I(N)[q(N - \frac{1}{2})/C + V_c - V_1 - V_2]. \quad (23)$$

Total power dissipated  $P_c$  is Eq. (23) summed over all  $N$ . The power conversion efficiency  $E$  is then defined as  $P_w/P_c$ , or

$$E = \frac{(V_1 + V_2) \sum_N I(N)}{\sum_N I(N)[q(N - \frac{1}{2})/C - V_r]}. \quad (24)$$

In the limit of large  $C$  where fluctuation voltages are small, Eq. (24) reduces to the appropriate ratio of battery voltage to passive voltage drop which is less than zero, the expected macroscopic result because no power conversion occurs for negligible fluctuation voltages.

Because of the error in distributing the voltages according to circuit capacitances, Yater's expression for conversion efficiency converges for large  $C$  to a ratio of capacitance values which is greater than zero. This result implies the physically unrealistic result that power conversion occurs for macroscopic circuits and can lead to erroneous conclusions about the allowable circuit capacitances.

## RESULTS

Extensive calculations using Eqs. (22) and (24) have been carried out to characterize the concept. Selected results are presented in Fig. 2 as power conversion efficiency versus system total capacitance  $C$ , and as dc power output normalized to  $G$  (the saturation current of the cold diode) versus system total capacitance  $C$ .

Let us first focus attention to the right-hand side of Fig. 2. Results for several values of

$V = V_1 + V_2$  and for  $K = 10^2$ ,  $T_c = 300^\circ\text{K}$ , and  $T_r = 1000^\circ\text{K}$  are shown there. Operation of the concept is as follows. As  $C$  decreases to below  $10^{-18}$  F, the fluctuation voltage due to  $N = 1$  becomes larger than  $V$  by greater than  $kT_c/q$ . The cold diode then is appreciably nonlinear and rectification occurs. Thus the dc power output increases as  $C$  decreases towards  $3.5 \times 10^{-18}$  F (right-hand lower corner of Fig. 2 shows this for  $V_1 + V_2 = -0.075$  V). However, there is a competing effect which prohibits unrestricted lowering of  $C$ ; the probability that one electron has sufficient energy to cross over the barrier of the cold diode and increase the circuit energy by  $q^2/2C$  drops exponentially as this energy increment becomes

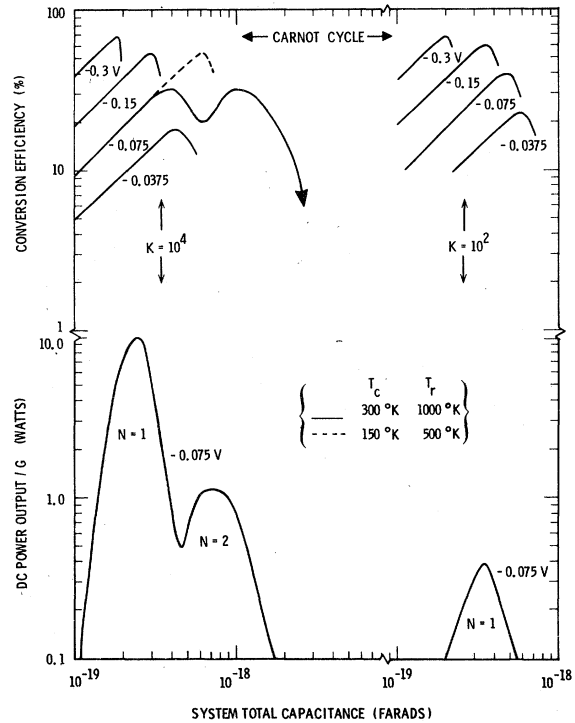


FIG. 2. Calculated results using the corrected equations derived in the present work. The conversion efficiency is shown in the upper half vs system (circuit) total capacitance for various bias voltages ( $V_1 + V_2$  of Fig. 1) and for two values of  $K$ . The lower half shows dc power output for the maximum observed case of  $V_1 + V_2 = -0.075$  V vs system (circuit) total capacitance. The dashed line shows results for lowering the temperature of the cold side while keeping the Carnot-cycle limit (70%) the same as for the solid-line results.

much larger than  $kT_c$ . Thus as  $C$  decreases further to below  $3.5 \times 10^{-18}$  F, the dc power output falls off. Thus the peak in power output occurs. Calculations show that the peak power is highest for  $V = -0.075$  for  $T_c = 300$  °K, and in general for  $V = -2kT_c/q$ . Any other value of  $|V|$  shifts the peak to lower power outputs, and to lower or higher  $C$  values for higher or lower  $|V|$  values, respectively. For instance,  $V = -0.3$  V drops the peak power by a factor of 3.

The results on the right-hand side of Fig. 2 for other values of  $V$  show that higher efficiencies can be obtained for higher  $|V|$  and lower  $C$  values, but, as mentioned, at the expense of power output. Note that peak conversion efficiency occurs for  $C$  values larger than those necessary for peak power output.

The left-hand side of Fig. 2 shows similar results, but for  $K = 10^4$ . The peak power output for  $N = 1$  goes up, but the conversion efficiency at peak power goes down. Also, the curves shift to lower capacitance. For values of  $K$  larger than  $10^4$  it was found that these trends continue. For  $K < 2$ , no power conversion occurs. Also, for  $K$  values larger than  $10^3$ , values of  $N$  greater than 1 have some rectification effects as seen in the left-hand side of Fig. 2, where a  $C$  value around  $7 \times 10^{-19}$  F with two electrons ( $N = 2$ ) causes rectification. The probability of  $N = 2$  is smaller, however, so the peak power output in Fig. 2 is seen to be much smaller than for  $N = 1$ . The probability for  $N > 2$  is so small for this case that no net dc power output is calculated.

The dashed line in Fig. 2 shows the results of decreasing the cold-side temperature while keeping the Carnot-cycle limit constant by lowering  $T_r$  also. All effects shift to higher  $C$  since the fluctuation voltages for rectification must be comparable to  $kT_c/q$ .

#### DISCUSSION

The behavior of the calculated results with  $K$ , the ratio of hot-side saturation current to cold-side saturation current, can be explained conceptually. Self-rectification of noise voltage by a nonlinear device, i.e., the rectification of a nonlinear-resistor's noise voltage by its own nonlinearities, cannot be used as a power source.<sup>2,4</sup> Therefore, since the power output must come from the temperature difference between the hot and cold sides, rectification must be on the cold side. The parameter  $K$  is a measure of the relative resistances of the diodes and determines how the fluctuation and circuit voltages divide between the hot and cold diodes. From Eqs. (6) and (7), for  $K \approx q(V_1 + V_2)(T_r - T_c)/2kT_cT_r$ , the voltages are

equally divided. In the case used for Fig. 2,  $K = 2$  is the dividing line. For  $K > 2$  rectification is primarily on the cold side and dc power output occurs. For  $K < 2$  rectification is primarily on the hot side and no dc power output occurs.

However,  $K$  cannot be simply increased because the impedance match between the hot and cold side becomes imbalanced. In fact, impedance imbalance is the primary reason the peak efficiency does not occur for the peak power output.

The proposed concept of power generation with rectification of fluctuation power is necessarily constrained to small power output per device. The quantum-mechanical limit<sup>5</sup> on available noise power for  $T_r - T_c = 700$  °K is  $1.4 \times 10^{-7}$  W. Because of the impedance mismatches necessary to cause rectification only on the cold side, full power output per device is constrained. Also, the assumption of appreciable heat transfer by conduction is questionable if less than maximum electrical output power is considered. Therefore, from a practical point of view it is necessary to consider only the maximum-power-output conditions. For maximum power output, the conversion efficiencies range from 24% for  $K = 10^4$  up to a maximum of 32% at  $K = 10^2$  and down again to 20% at  $K = 5$ . These efficiencies are less than one-half the Carnot cycle limit of 70% and are not of much practical significance. Attempts to enhance the conversion efficiency by changing circuit capacitance or bias voltage causes the available power per device to drop faster than the efficiency goes up.

#### CONCLUSIONS

Errors have been found in the equations used by Yater to calculate the power conversion of energy fluctuations in electrical circuits. The errors have been corrected and new calculated results are presented. The errors have little effect on Yater's calculations for the limited case of two identical diodes with vanishingly small capacitances. However, the corrected equations are shown to be more generally applicable and to converge in the limit of large circuit capacitances to the correct macroscopic result; Yater's equations, in particular, his conversion efficiency expression, do not. The performance of the energy-conversion concept is evaluated quantitatively and explained conceptually in terms of conventional electrical-circuit concepts.

The calculated results show that maximum conversion efficiency as defined and maximum power output do not occur for the same circuit capacitances, a result to be expected for circuits containing impedance mismatches with the definition

of power-conversion efficiency used. The maximum conversion efficiency for maximum power output is 32% for a temperature difference of 700 °K between the hot and cold sides of the circuit, the cold side being at 300 °K.

Changes in the circuit capacitance to increase conversion efficiency cause a drop in power output per device faster than efficiency increases.

Finally, since the results are presented in unnormalized form, it is easy to see that only non-linear circuits with total circuit capacitances of

the order of  $3 \times 10^{-19}$  F will produce maximum power output per device. This order of capacitance requires dimensions of the order of 50 Å or less.

#### ACKNOWLEDGMENTS

Helpful discussions with P. M. Richards, R. A. Kiehl, and K. W. Mitchell are deeply appreciated. This work was supported by the U. S. Department of Energy (DOE) under Contract No. AT(29-1)789.

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