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Efficiency at maximum power for an isothermal chemical engine with particle exchange at varying chemical potential

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Abstract. We calculate the efficiency at maximum power (EMP) of an isothermal chemical cycle in which particle uptake occurs at a fixed chemical potential but particle release takes place at varying chemical potential. We obtain the EMP as a function of $\Delta\mu/kT$, where $\Delta\mu$ is the difference between the highest and lowest reservoir chemical potentials and T is the absolute temperature. In the linear response limit, $\Delta\mu \ll kT$, the EMP tends to the expected universal value $1/2$.

Studies of the efficiency at maximum power (EMP) of an engine (thermal or chemical) are being considered important in the field of irreversible thermodynamics in recent years and results of general interest have been obtained [1]. These results are relevant to various fields in science and engineering, and impact on a wide range of disciplines, from macroscopic (irreversible) thermodynamics to the biophysics and biochemistry of nanosized systems such as, e.g., molecular motors. For a thermal engine, for which the Carnot cycle is the maximum-efficiency paradigm in the reversible limit, it has been established that the EMP for an irreversible cycle is universal and equals $e_c/2$, with e_c the Carnot efficiency, in the linear response limit [2–6]. For an isothermal chemical engine similar efforts have suggested that the EMP takes the universal value $1/2$ in linear response. Moreover, beyond linear response theory upper and lower bounds were derived, both of which converge to $1/2$ in the linear response limit [7]. The robustness of this value was recently tested in a specific implementation of a chemical engine, being a four-phase isothermal cycle in which particles are taken up at a fixed chemical potential and released at a fixed lower chemical potential. An EMP equal to $1/2$ was confirmed in the linear response regime [10].

In this manuscript we pose and answer the following fundamental questions. How is the EMP of a chemical cycle affected when the uptake or release of particles occurs at *varying chemical potential* instead of constant chemical potential? Is the EMP in

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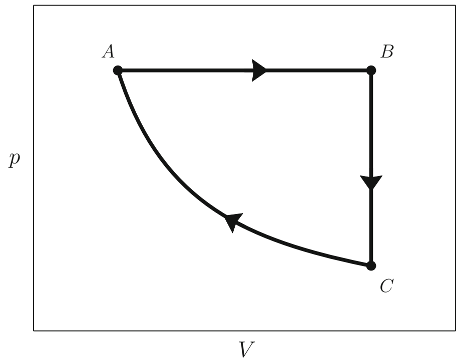

Fig. 1. Three-phase isothermal chemical cycle in a $p - V$ diagram. Phase AB consists of an isothermal and isobaric expansion with uptake of particles at constant chemical potential. Phase BC corresponds to an isovolumetric release of particles into chemical reservoirs at varying chemical potential. Phase CA represents an isothermal and isocardinal (constant particle number) compression. The enclosed area equals the total mechanical work.

the linear response regime possibly modified by this generalization, or is the universal value 1/2 recovered as might be expected? Our generalization is motivated by its analogous counterparts in the family of thermal engines, where it is natural to consider (non-Carnot) cycles with uptake and release of heat at *varying temperature*, instead of constant temperature (Carnot cycle).

For concreteness we take as working fluid an ideal gas of N particles in a volume V with s active degrees of freedom ($s = 3$ for a monoatomic gas, etc.). We recall that the chemical potential is then given by (in three dimensions)

$$\mu = kT \ln(\rho\Lambda^3), \tag{1}$$

with k Boltzmann's constant, T the absolute temperature and Λ the thermal de Broglie wavelength. For our purposes Λ is a constant.

The engine we study is the three-phase cycle shown in Figure 1. The process AB is an isothermal and isobaric expansion with uptake of ΔN particles from a reservoir at constant chemical potential μ_A. The number density ρ remains constant. The process BC is an isothermal and isovolumetric transformation in which ΔN particles are released at a chemical potential that *decreases* (because ρ decreases) from $\mu_B = \mu_A$ to μ_C. An isothermal compression, process CA, in which the particle number N is kept constant (and equal to N_A), closes the cycle. We first discuss properties of this cycle in the reversible limit and then proceed to calculate the EMP for the irreversible cycle.

The change in internal energy ΔU, the exchanged heat Q, the mechanical work W done on the gas (through the motion of a piston) and the chemical work input from a reservoir, W^{chem}, are given in Table 1 for each process. Energy conservation implies, for each process,

$$\Delta U = Q + W + W^{chem} = Q + W + \int \mu dN, \tag{2}$$

where the integral anticipates that μ depends on N during the particle release phase.

We recall that in a reversible isothermal chemical engine the chemical energy of particle exchange is entirely converted into useful mechanical work. Also some heat is taken up from a thermal reservoir, but the same amount of heat is released into the same reservoir. Therefore, the heat exchange is irrelevant and the efficiency η equals

Table 1. Overview of the thermodynamic quantities in the reversible cycle. For each phase of the cycle the change in internal energy ΔU, the mechanical work W, the chemical energy W^{chem} and the heat exchange Q are given. We have defined $\Delta\mu \equiv \mu_A - \mu_C > 0$ and use has been made of the equality $\Delta N/N_A = e^{\Delta\mu/kT} - 1$, derived by considering phase BC.

Phase	ΔU	W	W^{chem}	Q
AB	$\frac{s}{2}\Delta N\,kT$	$-\Delta N\,kT$	$\mu_A\Delta N$	$(\frac{s+2}{2}kT - \mu_A)\Delta N$
BC	$-\frac{s}{2}\Delta N\,kT$	0	$\left(kT - \mu_A - \frac{\Delta\mu}{e^{\Delta\mu/kT}-1}\right)\Delta N$	$\left(\mu_A - \frac{s+2}{2}kT + \frac{\Delta\mu}{e^{\Delta\mu/kT}-1}\right)\Delta N$
CA	0	$\frac{\Delta\mu}{e^{\Delta\mu/kT}-1}\Delta N$	0	$-\frac{\Delta\mu}{e^{\Delta\mu/kT}-1}\Delta N$
Total	0	$\left(\frac{\Delta\mu}{e^{\Delta\mu/kT}-1} - kT\right)\Delta N$	$\left(kT - \frac{\Delta\mu}{e^{\Delta\mu/kT}-1}\right)\Delta N$	0

unity in the reversible limit. A reversible engine, however, has zero power because a reversible cycle takes an infinitely long time.

In order to obtain nonzero power, we follow closely the procedure proposed earlier for a thermal cycle [8] and for a chemical cycle [9,10]. One considers that irreversible particle uptake (phase AB) and irreversible particle release (phase BC) each take a finite time, τ_1 and τ_2, respectively. Also in accord with earlier procedures, we consider that the particle current is governed by a (linear) transport law akin to Fick's law of diffusion,

$$\frac{dN}{dt} = \lambda(\mu - \mu^*), \tag{3}$$

where λ is a transport coefficient. The chemical potential μ is that of the reservoir and μ^* is an adjustable value with respect to which the power of the cycle can be maximized. The cycle is running between chemical potentials μ_A^* ($< \mu_A$) and μ_C^* ($> \mu_C$). The process CA is assumed to remain (quasi-)reversible and to take a (long but formally still finite) time $(q-1)(\tau_1+\tau_2)$ so that the cycle period is $q(\tau_1+\tau_2)$. The power P is the total mechanical work divided by this period. Assuming that $\mu - \mu^*$ is constant during a process, we obtain

$$P = \frac{\frac{1}{q}\left(\frac{\Delta\mu^*}{e^{\Delta\mu^*/kT}-1} - kT\right)}{\frac{1}{\lambda_1(\mu_A-\mu_A^*)} + \frac{1}{\lambda_2(\mu^*(\rho)-\mu(\rho))}}, \tag{4}$$

where $\Delta\mu^* \equiv \mu_A^* - \mu_C^*$ and λ_1 and λ_2 pertain to phases AB and BC, respectively. During phase AB we have constant values $\mu = \mu_A$ and $\mu^* = \mu_A^*$. We define $\mu_A - \mu_A^* \equiv x_1\,kT$. The difference $\mu^*(\rho) - \mu(\rho) \equiv x_2\,kT$ is also constant, while both $\mu(\rho)$ and $\mu^*(\rho)$ decrease during phase BC. This is why we make their density dependence explicit. Since the chemical potential of the working fluid in the cycle is continuous, also in B, we have $\mu_A^* = \mu^*(\rho_B)$.

The power can now be optimized with respect to x_1 and x_2. For calculational ease, one may choose instead as independent variables x and x_2, with $x\,kT \equiv \Delta\mu^* = \Delta\mu - (x_1+x_2)kT$. The requirement $\partial P/\partial x_2 = 0$ leads to the symmetry relation

$$\sqrt{\frac{\lambda_2}{\lambda_1}} = \frac{x_1}{x_2}, \tag{5}$$

while the requirement $\partial P/\partial x = 0$ leads to an equation, which, after substitution of (5), simplifies to the following expression that is independent of the transport coefficients,

$$\frac{\Delta\mu}{kT} = x + \frac{(e^x-1-x)(e^x-1)}{xe^x - e^x + 1}, \tag{6}$$

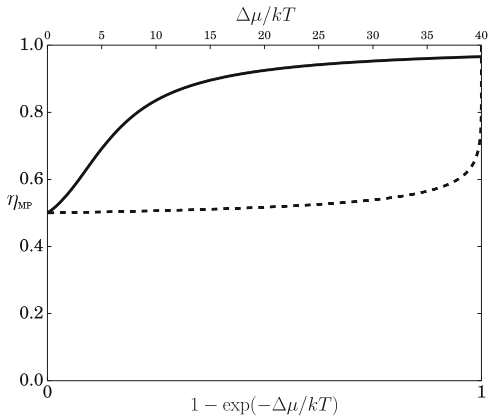

Fig. 2. The efficiency at maximum power (EMP), denoted by η_{MP}, is displayed as a function of $\Delta\mu/kT$ (solid upper curve) or as a function of $1-\exp(-\Delta\mu/kT)$ (dashed lower curve). The latter representation covers the entire physical range of $\Delta\mu/kT$. Clearly, $1/2 \leq \eta_{\text{MP}} \leq 1$.

which, when inverted, gives the optimal x as a function of $\Delta\mu/kT$. We note that for small $\Delta\mu/kT$, and therefore also small x, we obtain $\Delta\mu/kT \sim 2x$, where the symbol $\sim$ means "asymptotically equal to".

We now proceed to calculate the EMP, which is defined as the total work performed by the cycle divided by the available total chemical energy between uptake and release into the reservoirs, evaluated at maximum power,

$$\eta_{\text{MP}} = \frac{\left(1-\frac{x}{e^x-1}\right)}{1-\frac{\Delta\mu/kT}{e^{\Delta\mu/kT}-1}}, \tag{7}$$

where x is the function of $\Delta\mu/kT$ implied by (6). Asymptotic analysis for the linear regime leads to

$$\eta_{\text{MP}} = \frac{1}{2} + \frac{1}{48}\frac{\Delta\mu}{kT} + \mathcal{O}\left(\left(\frac{\Delta\mu}{kT}\right)^2\right) \tag{8}$$

and in the opposite limit, for large $\Delta\mu/kT$, we obtain

$$\eta_{\text{MP}} \sim 1 - \frac{kT}{\Delta\mu}. \tag{9}$$

The EMP versus $\Delta\mu/kT$, or versus the suitable alternative variable $1-\exp(-\Delta\mu/kT)$, is shown in Figure 2.

Remarkably, the precise way in which the cycle is made irreversible does not affect the EMP. In fact, the same η_{MP} as a function of $\Delta\mu/kT$ results if only one particle exchange process is made irreversible instead of two. Moreover, in that case it doesn't matter which phase, AB or BC, is made irreversible. In all cases exactly the same function results for the EMP versus $\Delta\mu/kT$, but the calculation with only one irreversible process is simpler because it features only one parameter with respect to which the power must be maximized, instead of two. This invariance can be understood mathematically from the observation that, in the calculation with two irreversible processes, the EMP is independent of the transport coefficient ratio λ_2/λ_1.

This kind of invariance holds also to some extent for the four-phase cycle in which particle uptake and release are assumed to happen at two different, but constant, chemical potentials [10]. In that cycle, for the special case of a linear transport law (without nonlinear corrections) the EMP equals 1/2, independently of $\Delta\mu/kT$ and independently of whether one or both particle exchange processes are made irreversible. However, this invariance is no longer guaranteed when nonlinear correction terms are present in the transport law [10].

Finally, a similar invariance holds for the irreversible thermal cycle considered by Curzon and Ahlborn [8], starting from the reversible Carnot cycle. Indeed, making only one isothermal phase of the Carnot cycle irreversible, instead of both, leads to the same EMP, as one can readily verify. This invariance, in the case of the thermal cycle, can be understood mathematically from the observation that the EMP is independent of the ratio of the two thermal conductivities involved.

In conclusion, we have considered a fairly generic isothermal chemical cycle in which particles can be exchanged at varying chemical potential. This cycle generalizes the earlier proposed paradigm of an isothermal chemical cycle in which particle uptake is performed at a constant chemical potential and particle release is also performed at a constant (but lower) chemical potential [10]. We have derived the EMP for the cycle. It is a nontrivial function of the reduced chemical potential difference $\Delta\mu/kT$. The EMP takes the (presumably universal) value 1/2 in the linear response limit ($\Delta\mu/kT \ll 1$) and slowly approaches the maximum achievable efficiency, 1, in the limit of large $\Delta\mu/kT$.

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