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# Educational Note: Enumerating Thermal Cycles

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## Motivation

When young undergraduate students of natural sciences or chemistry meet thermodynamics for the first time they are, according to the experience of the second author, overwhelmed by new insights and concepts. One particular difficulty seems to be the concept of Entropy, nowadays very often introduced in an axiomatic manner [1, 2, 3, 4], leaving the student with an uneasy feeling about this peculiar and abstract entity.

Sometimes on the other hand Entropy is approached by thermal cycles, especially by working out Carnot's Cycle [5, 6]. It seems that most chemistry students think that this is the only important cycle and sometimes even think that there are no others.

In fact there are, of course, infinitely many different cycles and quite a few cycles with three or four steps, one of which is Carnot's Cycle, others describing the Diesel- or Otto-Processes [7], which are important to estimate the efficiency of reciprocating engines.

In this paper - aimed at graduate students in a second course on thermodynamics - we enumerate all thermal cycles with three or four steps using isothermal, isobaric, isochoric and adiabatic processes basically using a modification of Pólya's Theorem, which can be conveniently introduced on this occasion.

One could also include polytropic processes [7] – a nice extension which is left to the reader.

A Mathematica Notebook (*kreisprozesse.nb*) is freely accessible under www.mathe2.uni-bayreuth.de/match/online/links.html#kpnb which not only constructs these cycles giving all the points of the cycle in the $p$-$V$-plane, but also calculates heat, work and entropy-changes for each single step using the equations for an ideal gas.

## Processes and Cycles

We construct cycles in a $p$-$V$-diagram using the following processes :

| Designator | Type of Process | Equation |
|---|---|---|
| $p$ | isobaric | $V_1 / T_1 = V_2 / T_2$ |
| $Q$ | adiabatic | $p_1 V_1{}^k = p_2 V_2{}^k$ |
| $T$ | isothermal | $p_1 V_1 = p_2 V_2$ |
| $V$ | isochoric | $p_1 / T_1 = p_2 / T_2$ |

(A polytropic process is described by $p_1 V_1{}^x = p_2 V_2{}^x$ with $x \neq c_p / c_v$ .)

So any cycle is given by an ordered set $C = (a, b, c, d, \ldots)$ with $a \in \{p,Q,T,V\}$, $b \in \{p,Q,T,V\}$, $c \in \{p,Q,T,V\}$, $d \in \{p,Q,T,V\}$ and so on. The question is, how many $C$ with exactly three or four elements exist?

To be meaningful there are restrictions on $C$.

Shifting the elements of $C$ to the left or right does not change the cycle in a $p$-$V$-diagram:

$$(p, Q, p, T) = (T, p, Q, p) = (p, T, p, Q) = (Q, p, T, p).$$

This is equivalent to the statement that a cycle of length $m$ is invariant under the operations of the pure rotation group $C_m$ (the cyclic group of order $m$).

Another restriction is that no two equal letters may follow each other. This would be a mere prolongation of the former process and consequently a pattern like

$$(p, p, T, Q)$$

is forbidden. In fact this process is equivalent to $(p, T, Q)$.

This in turn means with respect to the shifting process that the last letter must be different from the first one.

So we have to find all cycles which obey these rules. As noted later, however, it is sometimes possible to draw distinct diagrams in the $p$-$V$-plane corresponding to the same cycle. Furthermore, occasionally a cycle satisfying the stated properties seems to correspond to no closed cycle in the $p$-$V$-plane and some cycles which can be realised in the $p$-$V$-plane may be infeasible for technical reasons.

## The Method of Solution

Without the restriction that no two consecutive processes be identical, the problem could be solved by a routine application of Pólya's Theorem. Pólya's paper [9], which has some 110 pages, is often cited but presumably rarely read and, in spite of its importance, it took some 50 years for an English translation to appear [10]. His basic ideas of counting entities which are invariant under application of the elements of a given (symmetry) group are outlined in a quite readable form in short in [11]. The only ingredient used there is the Cauchy-Frobenius Lemma, which is lucidly explained in [12]. In fact Pólya had been anticipated by Redfield [13] and the theorem is often called the Redfield-Pólya Theorem.

Pólya's method consists of two parts. First a polynomial in several variables (here denoted by $s_1, s_2, \ldots$) is formed and then substitutions are made for the $s_i$. Pólya called the polynomial the *cycle-index*, but Redfield called it the *group reduction function*. An element $g \in G$ belonging to a symmetry $G$ acting on a set $X$ splits the elements of $X$ into cycles of various lengths. The *cycle-index* $Z_G(s_1, s_2, \ldots)$ is defined by

$$Z_G(s_1, s_2, \ldots) = \frac{1}{|G|} \sum_{g \in G} s_1^{j_1(g)} s_2^{j_2(g)} \ldots s_m^{j_m(g)},$$

where $j_i(g)$ denotes the number of cycles of length $i$ in the splitting and $m$ is the size of $X$. In the case of the cyclic group $C_m$ of order $m$, the length of every cycle must be a divisor of $m$ and it is well-known that the cycle index $Z_{C_m}(s_1, s_2, \ldots, s_m)$ in this case is

$$Z_{C_m}(s_1, s_2, \ldots, s_m) = \frac{1}{m} \sum_{r|m} \phi(r) s_r^{m/r}$$

where $r|m$ means $r$ divides $m$ and $\phi$ is Euler's function defined by $\phi(1) = 1$ and for $r = 2, 3, \ldots$ , $\phi(r)$ is the number of integers $s$ between 1 and $r$ inclusive which are relatively prime to $r$ (i.e. the greatest common divisor of $s$ and $r$ equals 1). The values of $\phi$ (see Table 1) can be obtained either from the definition or from the fact that (see, for example, [14, p77])

$$\phi(r) = r(1 - 1/p_1)(1 - 1/p_2) \ldots (1 - 1/p_k)$$

where $p_1, p_2, \ldots, p_k$ are all the distinct primes dividing $r$. So, for example,

$$\phi(12) = 12(1 - 1/2)(1 \quad 1/3) \quad 4.$$

**Table 1 Euler's function**

| $r$ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\phi(r)$ | 1 | 1 | 2 | 2 | 4 | 2 | 6 | 4 | 6 | 4 | 10 | 4 |

In the case of four types of processes, the substitution $s_r = p^r + Q^r + T^r + V^r$ in the cycle index produces the generating function

$$\frac{1}{m} \sum_{r|m} \phi(r)(p^r + Q^r + T^r + V^r)^{m/r}.$$

When this is expanded explicitly into the form of a power series

$$\sum_{m_1+m_2+m_3+m_4=m} e(m_1,m_2,m_3,m_4)p^{m_1}Q^{m_2}T^{m_3}V^{m_4} ,$$

the coefficient $e(m_1,m_2,m_3,m_4)$ is the number of cycles of length $m = m_1 + m_2 + m_3 + m_4$ which contain $m_1$ processes of type $p$, $m_2$ of type $Q$, $m_3$ of type $T$ and $m_4$ of type $V$.

With $n$ types $A_1, A_2, \ldots, A_n$ of processes, the corresponding substitution is

$$s_r = A_1^r + A_2^r + \ldots + A_n^r .$$

The total number $e_{m,n}$ of cycles of length $m$ is obtained by setting $A_1 = A_2 = \ldots = A_n = 1$, so that $s_r = n$ for all $r$ and, therefore,

$$e_{m,n} = \frac{1}{m}\sum_{r|m}\phi(r)n^{m/r} .$$

So, with cycles of length 3,

$$e_{3,n} = \frac{1}{3}\{\phi(1)n^3 + \phi(3)n\} = \frac{1}{3}\{n^3 + 2n\} .$$

In particular, $e_{3,3} = 11$ and $e_{3,4} = 24$ .

With cycles of length 4 and $n$ types of processes we obtain

$$e_{4,n} = \frac{1}{4}\{\phi(1)n^4 + \phi(2)n^2 + \phi(4)n\} = \frac{1}{4}\{n^4 + n^2 + 2n\} ,$$

e.g. $e_{4,4} = 70$ .

But this does not take into account that no two equal types of processes are allowed to follow each other.

With restrictions on which types of processes may immediately follow which, the above calculations need to be modified and smaller numbers will be obtained. With cycles of length three, simple arguments can be used. Each element in a three cycle is adjacent to the other two, hence, if the only restriction is that no type of process is next to itself, then each of the three types in the cycle must be different. Thus there are $\binom{n}{3}$ ways to choose the three elements and, if cycle $(a, b, c)$ is a regarded as different from $(a, c, b)$, then there are $2\binom{n}{3}$ different cycles (see the $m = 3$ column in Table 3).

For cycles of size $m \geq 4$, however, such a simple argument is not available. Instead, a modification of Pólya's Theorem can be used in which each $s_r^{m/r}$ in the cycle index is replaced by the trace of an appropriate matrix. The method is explained by Lloyd [8] who considered the problem of enumerating necklaces using beads of several different colours where there are restrictions on which colours may appear next to which. By changing the words (*bead* $\rightarrow$ *process* and *colour* $\rightarrow$ *type of process*) the ideas in that paper can be applied to the present problem.

The matrix $T$ used in [8] will be called $M$ here in order to avoid confusion with the isothermal process. Also, Lloyd used the dihedral group $D_m$ but using the cyclic group $C_m$ only requires replacing the cycle index of the dihedral group by that of the cyclic group. With the dihedral group, a cycle such as $(p, V, Q, T)$ is regarded as the same as the reverse order cycle $(p, T, Q, V)$ whereas they are counted as separate cycles when the cyclic group is used. Lloyd's paper consists solely of theory and is not illustrated with any examples.

For $n$ types $A_1, A_2, \ldots, A_n$ of processes, the $n \times n$ matrices $M$, $M_r$ and $B$ are defined by (see [8]):

entry $(M)_{ij} = A_j$ if process $A_j$ may immediately follow process $A_i$ and $(M)_{ij} = 0$ if not;
entry $(M_r)_{ij} = (M_{ij})^r$, $r = 1, 2, \ldots$;
entry $(B)_{ij} = 1$ if $(M)_{ij} \neq 0$ and $(B)_{ij} = 0$ if $(M_{ij}) = 0$.

So, for example, with four types $p, Q, T, V$ of processes where no type is adjacent to itself (and with no other restrictions on adjacency) the matrices are:

$$M = \begin{bmatrix} 0 & Q & T & V \\ p & 0 & T & V \\ p & Q & 0 & V \\ p & Q & T & 0 \end{bmatrix}, \quad M_r = \begin{bmatrix} 0 & Q^r & T^r & V^r \\ p^r & 0 & T^r & V^r \\ p^r & Q^r & 0 & V^r \\ p^r & Q^r & T^r & 0 \end{bmatrix}, \quad B = \begin{bmatrix} 0 & 1 & 1 & 1 \\ 1 & 0 & 1 & 1 \\ 1 & 1 & 0 & 1 \\ 1 & 1 & 1 & 0 \end{bmatrix}.$$

The substitution required in the cycle index in order to obtain a generating function for the present case with adjacency restrictions is, for $r = 2, 3, \ldots$ ,

$$s_r = \operatorname{tr}(M_r^{m/r}),$$

so the required generating function is

$$\frac{1}{m}\sum_{r|m}\phi(r)\operatorname{tr}(M_r^{m/r}).$$

The total number of cycles is again obtained by putting $A_1 = A_2 = \ldots = A_n = 1$. Each $M_r$ then becomes equal to $B$. Hence:

**Theorem** With $n$ types of processes, the total number $e_m(B)$ of cycles of length $m$ with adjacency restrictions specified by the matrix $B$ is, for $m = 2, 3, 4, \ldots$ and $n = 1, 2, 3, \ldots$ ,

$$e_m(B) = \frac{1}{m}\sum_{r|m}\phi(r)\operatorname{tr}(B^{m/r}).$$

It should be noted that some of the cycles included in this count do not use all the types of processes. For example, with four types $p$, $Q$, $T$, $V$, the number $e_4(B)$ would include cycles such as ( $p$, $T$, $p$, $V$ ) in which $Q$ is not used. Such cycles are wanted in the enumeration.

## Thermal Cycles with Four Types of Processes and Lengths Three, Four and Five

In this case, the matrix $B$ is the $4 \times 4$ matrix above and to solve the cycle enumeration problem, a knowledge of its powers is required. The first five are:

$$\begin{bmatrix} 0 & 1 & 1 & 1 \\ 1 & 0 & 1 & 1 \\ 1 & 1 & 0 & 1 \\ 1 & 1 & 1 & 0 \end{bmatrix}, \begin{bmatrix} 3 & 2 & 2 & 2 \\ 2 & 3 & 2 & 2 \\ 2 & 2 & 3 & 2 \\ 2 & 2 & 2 & 3 \end{bmatrix}, \begin{bmatrix} 6 & 7 & 7 & 7 \\ 7 & 6 & 7 & 7 \\ 7 & 7 & 6 & 7 \\ 7 & 7 & 7 & 6 \end{bmatrix}, \begin{bmatrix} 21 & 20 & 20 & 20 \\ 20 & 21 & 20 & 20 \\ 20 & 20 & 21 & 20 \\ 20 & 20 & 20 & 21 \end{bmatrix}, \begin{bmatrix} 60 & 61 & 61 & 61 \\ 61 & 60 & 61 & 61 \\ 61 & 61 & 60 & 61 \\ 61 & 61 & 61 & 60 \end{bmatrix}.$$

The corresponding traces are:

$$\text{tr}(B) = 0, \quad \text{tr}(B^2) = 12, \quad \text{tr}(B^3) = 24, \quad \text{tr}(B^4) = 84, \quad \text{tr}(B^5) = 240.$$

For cycles of lengths 3, 4 and 5, therefore, with four types of processes, the theorem can be applied to conclude that:

$$e_3(B) = \frac{1}{3}\{\phi(1)\,\text{tr}(B^3) + \phi(3)\,\text{tr}(B)\} = \frac{1}{3}\{(1\times 24) + (1\times 0)\} = 8;$$

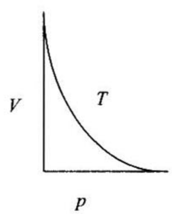
$$e_4(B) = \frac{1}{4}\{\phi(1)\,\text{tr}(B^4) + \phi(2)\,\text{tr}(B^2) + \phi(4)\text{tr}(B)\} = \frac{1}{4}\{(1\times 84) + (1\times 12) + (2\times 0)\} = 24;$$

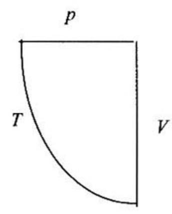
$$e_5(B) = \frac{1}{5}\{\phi(1)\,\text{tr}(B^5) + \phi(5)\,\text{tr}(B)\} = \frac{1}{5}\{(1\times 240) + (4\times 0)\} = 48.$$

These numbers agree with those found by the Mathematica program already mentioned. The program yields 8 cycles of length 3:

$$\{(p, T, V), (p, T, Q), (p, V, T), (p, V, Q), (p, Q, T), (p, Q, V), (T, V, Q), (T, Q, V)\}.$$

However, a close consideration shows that, for example, $(p, T, V)$ and $(p, V, T)$ are the same cycles, but gone through the other way round. This leaves effectively only four 3-cycles to be considered. Furthermore there is a certain ambiguity as to how to draw a cycle. For example it could well be discussed in the classroom whether the cycles $(V, p, T)$



are equivalent. Of course they are not, giving again a total of eight different cycles – but this has nothing to do with the enumeration process.

One of the calculations above shows that there are 24 cycles of length 4; the cycles themselves can be found by using the Mathematica program which yields:

$$\{(p, T, p, T), (p, T, p, V), (p, T, p, Q), (p, T, V, T), (p, T, V, Q), (p, T, Q, T),$$
$$(p, T, Q, V), (p, V, p, V), (p, V, p, Q), (p, V, T, V), (p, V, T, Q), (p, V, Q, T),$$
$$(p, V, Q, V), (p, Q, p, Q), (p, Q, T, V), (p, Q, T, Q), (p, Q, V, T), (p, Q, V, Q),$$
$$(T, V, T, V), (T, V, T, Q), (T, V, Q, V), (T, Q, T, Q), (T, Q, V, Q), (V, Q, V, Q)\}.$$

The reader may care to draw closed cycles in the $p$-$V$-plane corresponding to these 24 cycles in a clockwise manner ( this corresponds to transferring heat to work ). This can be done for 23 of the cycles, but it does not seem to be possible to obtain a closed cycle for number 7, $(p, T, Q, V)$ while a counter-clockwise cycle is perfectly possible.

Carnot's cycle is $(T, Q, T, Q)$, number 22, which is technically hardly feasible (7) due to the high pressures involved. The program gives the entropy-changes for the single steps

$$\left(\log\left[\frac{V_1}{V_2}\right], 0, \log\left[\frac{V_2}{V_1}\right], 0\right)$$

summing up to zero as it must be.

Further cycles may be mentioned

| | | |
|---|---|---|
| Diesel cycle | : | $(p, Q, V, Q)$ |
| Otto cycle | : | $(V, Q, V, Q)$ |
| Ackeret-Keller cycle | : | $(p, T, p, T)$ |
| Joule cycle | : | $(p, Q, p, Q)$. |

The main difference between a diesel and normal fuel engine is the retardation of combustion so that the expansion proceeds at constant pressure. This needs a more stable construction, but gives higher efficiencies.

## Thermal Cycles with Four Types of Processes and Length *m*

It is not difficult to obtain an explicit expression for the trace $\mathrm{tr}(B^t)$ of $B^t$ for any $t = 1, 2, \ldots$ and any $n$. The details for the case $n = 4$ are now given.

The simple structure of $B$ carries over to its powers. For each $t = 1, 2, \ldots$ all the diagonal entries of $B^t$ are identical and so are all the off-diagonal entries. Furthermore, if $t$ is odd then the off-diagonal entries are 1 greater than the diagonal entries, but if $t$ is even then they are 1 less.

Let $a_t$ denote the common diagonal entries of $B^t$ and $b_t$ the common off-diagonal entries. Then, since $B^{t+1} = BB^t$,

$$\begin{bmatrix} a_{t+1} & b_{t+1} & b_{t+1} & b_{t+1} \\ b_{t+1} & a_{t+1} & b_{t+1} & b_{t+1} \\ b_{t+1} & b_{t+1} & a_{t+1} & b_{t+1} \\ b_{t+1} & b_{t+1} & b_{t+1} & a_{t+1} \end{bmatrix} = \begin{bmatrix} 0 & 1 & 1 & 1 \\ 1 & 0 & 1 & 1 \\ 1 & 1 & 0 & 1 \\ 1 & 1 & 1 & 0 \end{bmatrix} \begin{bmatrix} a_t & b_t & b_t & b_t \\ b_t & a_t & b_t & b_t \\ b_t & b_t & a_t & b_t \\ b_t & b_t & b_t & a_t \end{bmatrix}.$$

Equating the (1, 1) and (1, 2) entries on both sides, it follows that

$$a_{t+1} = 3b_t, \qquad (1)$$

$$b_{t+1} = a_t + 2b_t. \qquad (2)$$

These relations enable values of $a_t$, $b_t$ and $\mathrm{tr}(B^t) = 4a_t$ to be calculated recursively, but explicit expressions can also be obtained. Replacing $t$ by $t + 1$ in (2) gives

$$b_{t+2} = a_{t+1} + 2b_{t+1}. \qquad (3)$$

Then eliminating $a_{t+1}$ between (1) and (3) leads to

$$b_{t+2} - 2b_{t+1} - 3b_t = 0.$$

This is a standard type of recurrence relation (second order linear homogeneous with constant coefficients) discussed in, for example, Barnett [15, Chap. 5]. It has a solution of the form

$$b_t = \alpha\lambda_1^t + \beta\lambda_2^t$$

where $\lambda_1$ and $\lambda_2$ are the roots of the auxiliary equation

$$\lambda^2 - 2\lambda - 3 = 0,$$

and $\alpha$ and $\beta$ are constants which can be evaluated by using the initial conditions $b_1 = 1$ and $b_2 = 2$.

(Some readers may be more familiar with solving analagous differential equations. The corresponding differential equation here is $\ddot{x} - 2\dot{x} - 3x = 0$ for which the solution takes the form $x(t) = \alpha\, e^{\lambda_1 t} + \beta\, e^{\lambda_2 t}$.)

It is, therefore, easy to deduce that

$$b_t = \frac{1}{4}\{3^t - (-1)^t\},$$

$$a_t = \frac{3}{4}\{3^{t-1} - (-1)^{t-1}\},$$

$$\mathrm{tr}(B^t) = 4a_t = 3\{3^{t-1} - (-1)^{t-1}\}.$$

Although these explicit solutions can be used to calculate values for any given $t$, in order to build up a table, it is easier to use the fact that the quantities satisfy the following relations:

$$b_{t+1} = 3b_t + (-1)^t,$$

$$a_{t+1} = 3\{a_t - (-1)^t,$$

$$\mathrm{tr}(B^{t+1}) = 3\{\,\mathrm{tr}(B^t) - 4(-1)^t\,\}.$$

Values of the traces $\mathrm{tr}(B^t)$ are given in the $n = 4$ row of Table 2.

## Thermal cycles with *n* members and length *m*

The details here are exactly parallel to the case $n = 4$. The starting matrix $B$ is now $n \times n$ but, as before, all diagonal entries equal 0 and all off-diagonal entries equal 1. The coefficients 3 and 2 in equations (1) and (2) change to $n-1$ and $n-2$ respectively, but the new relations

$$a_{t+1} = (n-1)b_t,$$
$$b_{t+1} = a_t + (n-2)b_t$$

can be solved in exactly the same way to get

$$b_t = \frac{1}{n}\{(n-1)^t - (-1)^t\},$$
$$a_t = \frac{n-1}{n}\{(n-1)^{t-1} - (-1)^{t-1}\} = b_t + (-1)^t,$$
$$\mathrm{tr}(B^t) = na_t = (n-1)\{(n-1)^{t-1} - (-1)^{t-1}\}.$$

In this general case, the traces satisfy

$$\mathrm{tr}(B^{t+1}) = (n-1)\{\mathrm{tr}(B^t) - n(-1)^t\}.$$

Values of the traces for $n = 1, 2, 3, \ldots$ and $t = 2, 3, 4, \ldots$ are given in Table 2 and values of the numbers $e_m(B)$ in Table 3.

**Table 2 Values for tr($B^t$) where $B$ is $n \times n$**

| $n \cdot\cdot t$ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2 | 0 | 2 | 0 | 2 | 0 | 2 | 0 | 2 | 0 | 2 |
| 3 | 0 | 6 | 6 | 18 | 30 | 66 | 126 | 258 | 510 | 1026 |
| 4 | 0 | 12 | 24 | 84 | 240 | 732 | 2184 | 6564 | 19680 | 59052 |
| 5 | 0 | 20 | 60 | 260 | 1020 | 4100 | 16380 | 65540 | 262140 | 1048580 |
| 6 | 0 | 30 | 120 | 630 | 3120 | 15630 | 78120 | 390630 | 1953120 | 9765630 |

**Table 3 Numbers $e_m(B)$ of cycles of length $m$ with $n$ types of processes**

| $n \backslash m$ | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2 | 1 | 0 | 1 | 0 | 1 | 0 | 1 | 0 | 1 |
| 3 | 3 | 2 | 6 | 6 | 14 | 18 | 36 | 58 | 108 |
| 4 | 6 | 8 | 24 | 48 | 130 | 312 | 834 | 2192 | 5934 |
| 5 | 10 | 20 | 70 | 204 | 700 | 2340 | 8230 | 29140 | 104968 |
| 6 | 15 | 40 | 165 | 624 | 2635 | 11160 | 48915 | 217040 | 976887 |

## Conclusion

This paper considers the problem of enumerating the number of closed loops in the $p$-$V$-plane consisting of given parts and representing thermal cycles.

Carnot's cycle, well known to students of natural sciences or chemistry is only one out of about 24 cycles having four steps which can be constructed using isothermal, isochoric, isobaric and adiabatic processes.

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