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Magic Squares and the Mathematics of Thermodynamics

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Abstract

Two similar 'magic squares' have recently been proposed as a shorthand method for the mathematics of thermodynamics. It is based on neighborhood relations between thermodynamic parameters. 'Magic squares' were born in China more than two thousand years ago and were an intriguing mathematical curiosity. A 'magic square' reappeared in Greece as a 'physicochemical magic square', while during renaissance a 'magic square' ended up in art, and, finally, thanks to Max Born, it showed up in thermodynamics. This last type of magic square, was used to solve a problem that intrigued P.W. Bridgam in his younger years, i.e., how to derive in a rather easy way the multifarious relations of Thermodynamics. Actually, Max Born 'some days' before the birth of quantum mechanics got involved in a series of studies in thermodynamics, who tied his name to the name of a relatively unknown mathematician, C. Carathéodory. One of the present two forms of thermodynamic 'magic square' allows to introduce and solve the Massieu functions and, thus, let get us in touch with this nearly unknown French scientist, F.J.D. Massieu.

Introduction

To the old Chinese (ca., 2200 B.C. [1, 2]) is credited the startling discovery that the first nine digits of the number system disposed in a square gave rise to strange properties that rendered the figure a 'magic square'. It should here be underlined that Chinese did not know the concept of zero, which was born in India 2800 years later [3]. The properties of this magic square are: the sum of the numbers along the columns, the rows, the diagonal and the anti-diagonal is always fifteen (the so-called magic constant), the sum of all numbers is $15 \cdot d = 45$, where d is the dimension of the square. Dividing 45 by 9, the number of digits, one obtains the number, 5, halfway between 9 and 1, and which occupies the middle cell, while the even numbers are on the corners, and the remaining odd numbers are on the sides, i.e.,

4	9	2
3	5	7
8	1	6

All four lines through the central 5 are in arithmetical progression, with differences 1, 2, 3, 4, rotating anti-clockwise from 6-5-4 to 9-5-1. The sum of the squares of the 1st and 3rd columns equal 89, while the same sum for the middle column gives 107 = 89 + 18. The squares of the numbers in the rows sum to 101, 83, 101, and 101 - 83 = 18. Further, $492^2 + 357^2 + 816^2 = 294^2 + 753^2 + 618^2$, and the same pattern is true for the columns, and for the diagonals (456, 978, 231). There are just 8 ways in which the magic total can be made by adding 3 of the integers 1 to 9, and each of these 8 ways occurs once in the square. The original ancient Chinese form of the magic square, known as lo-shu, [1, 2] was a combination of cyclic and acyclic graphs (Figure 1), and, actually this is the first 'intriguing' appearance of graphs in a mathematical subject. In these graphs the black vertices represent feminine even numbers and open circles masculine odd numbers.

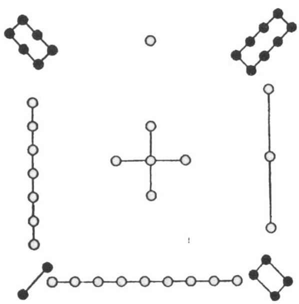
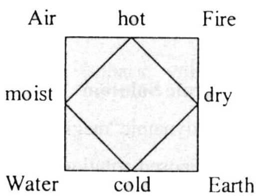


Figure 1. The ancient Chinese form for the magic square

It is told in the *'I-king'*, or *Book of Permutations*, that this 'magic square' (we could say 'magic graph') was written upon a back of a tortoise, which appeared to the emperor Yu when was embarking on the yellow river. It is also told that this emperor was an hydraulic engineer. The 'I-king' is often called the oldest of the Chinese classics, and the first European edition of this book appeared at Frankfurt in 1724. The magic square was known to the Neo-Platonists of the third century of this era, and it fascinated Arab mathematicians and alchemists around the 8^{th} -10^{th} century, and many others [4], later on in Europe, like Luca Pacioli, Fermat, and even Leibniz, who was highly interested in Chinese mathematics, having written a book on the subject, *Philosophia Sinensium* [1, 2]. The renaissance mathematician Luca Pacioli (1445-1514), a friend of Leonardo da Vinci, left an unfinished manuscript, *De Viribus Quantitatis*, in which are reported other magic squares. The influence of Pacioli, can be seen in a celebrated engraving of A. Dürer entitled, *the Melancholia*, where a 4x4 magic square with magic constant 34 is engraved, and in which, in the last row, can be read 1514, the year the engraving was done and the year of the death of Luca Pacioli. The rows of this magic square are: 16, 3, 2, 13; 5, 10, 11, 8; 9, 6, 7, 12; 4, 15, 14, 1. Pacioli wrote in 1494 the most influential algebra book of the period, *Summa de Arithmetica, Geometrica, Proportioni et Proportionata,* known as *Summa*, the first mathematics textbook to overshadow 1202 Fibonacci's *Liber Abaci* [2].

We will not follow the history of the magic squares, as our subject is more in keeping with the 3x3 magic square. Let us go back to the old Greeks, and check for the existence of another 3x3 'magic square', a 'chemical' one, first conceived by Aristotle, and worshipped by his followers, practically, till the advent of modern chemistry. Aristotle took a set of four elements as the basis of the material world: {Fire, Air, Water, Earth}, as well a set of four primary qualities {moist, dry, hot, cold}. Each element has assigned two properties, four combinations being possible: hot and dry assigned to fire, hot and moist to air, cold and fluid to water, and cold and dry to earth [4, 5]. Expressing it diagrammatically the following 'magic square' was obtained



This can surely be considered the very first periodic table of the elements, which lasted for nearly twenty centuries. The previous relations between elements and properties could be written in the following modern functional way (using the first letter): A = A(h, m); F = F(d, h); E = E(c, d), and W = W(m, c). This magic square allowed column and row transmutations, i.e., elements may pass into one another through the medium of that quality on the same column or row, i.e., which they posses in common. Thus, water can become earth through the medium of cold, earth can become fire through the medium of dry, and so on. A fifth immaterial element was added, which was called as the quintessence (the central number in the Chinese magic square), occupying the central position in the square, and which corresponds with the ether. Magic squares could have influenced XIX century chemists in shaping the periodic table of the elements with its well-known regularities, and which originally had the form of a square rather than the actual form more similar to a rectangle [5]. Thus, a strange Chinese curiosity from 2200 BC ended up 'shaping' old and modern chemistry.

Another magic square has been rediscovered in recent times, but in thermodynamics and with very interesting and helpful properties [6-8]. Actually, it seems that the idea of such a magic thermodynamic square came out of the fertile mind of Max Born. It is, in fact, told [9] that, in 1929, Max Born used, privately, a mnemonic square to derive the Maxwell relations in a straightforward way. But it was only in 1935 that such a square made its first appearance in the literature in a paper by Koenig [10]. It should here be reminded that a more impressive and easily traceable contribution to thermodynamics came from Max Born during those same years, and just short before the birth of quantum mechanics. In 1921 three fundamental papers by M. Born appeared in the literature [11-13] to support and strengthen what was known by very few people as the *axiomatic thermodynamics* developed by a friend of his, the mathematician Constantin Carathéodory, who in 1909 grounded this branch of thermodynamics, and in 1925, only after the interest awakened by Born papers, wrote a second and final piece to the subject [14-16].

The Problem and the Bridgam algebraic Solution

Before coming back to our thermodynamic 'magic square' let us talk about the problem we are interested in, and one of the proposed solutions, the algebraic solution by Bridgam. The problem consists in deriving a scheme of shorthand notation for a wide variety of thermodynamic relationships. In this section we will center our attention on the solution devised by P.W. Bridgam in 1914 short after his Ph.D. [17-19], and well before he became famous for his high pressure studies for which he earned the Nobel prize in physics in 1945, and also well before his less famous but fundamental studies in dimensional analysis [20, 21]. Actually Bridgam, starting from the late twenties, got interested also in the philosophy of physics, and wrote very interesting and illuminating books on the subject, like the 'Logic of modern physics' (1927), 'The Nature of Physical Theory' (1936), and 'The Nature of Thermodynamics' (1941). An interesting and intriguing contribution in this field continues to be the 'relativistic' definition Bridgam gave of scientific method: *scientific method is just what working scientists do, ..., is something talked about by people standing on the outside and wondering how the scientists manages to do it,....., and there are as many scientific methods as there are individual scientists.* But let us come back to the shorthand method proposed by Bridgam and centered on the properties of mathematical functions known as Jacobians, which are defined as follows,

$$J(x,y) = \partial(x,y)/\partial(\alpha,\beta) = \begin{vmatrix} (\partial x/\partial\alpha)_\beta & (\partial y/\partial\alpha)_\beta \\ (\partial x/\partial\beta)_\alpha & (\partial y/\partial\beta)_\alpha \end{vmatrix} = (\partial x/\partial\alpha)_\beta(\partial y/\partial\beta)_\alpha - (\partial x/\partial\beta)_\alpha(\partial y/\partial\alpha)_\beta \quad (1)$$

Reminding the following properties of the Jacobians,

$$J(x,y) = - J(y,x) \;;\quad (\partial y / \partial x)_z = J(y,z) / J(x,z) \;;\quad J(\alpha,\beta) = 1 \quad (2)$$

and rewriting the second of the three properties of eq. 2 with the following shorthand notation, we obtain,

$$(\partial y / \partial x)_z = (\partial y)_z / (\partial x)_z : \; (\partial y)_z = J(y, z), \text{ and } (\partial x)_z = J(x,z) \quad (3)$$

Now, (i) choosing $T = \alpha$, and $P = \beta$, (ii) expressing the results in terms of the three experimental properties (here, α = isobaric volume expansivity, and κ = isothermal compressibility),

$$(\partial V/\partial T)_P = \alpha V \;;\; (\partial V/\partial P)_T = - \kappa V \;;\; C_p = (\partial H/\partial T)_P = T(\partial S/\partial T)_P \quad (4)$$

(iii) using the fundamental principles of thermodynamics, inclusive the Maxwell relations, an entire set of thermodynamic relationships can be obtained, among which (eq. 1 is here the key equation, high numbered eqs. normally use results from the lower numbered eqs.):

1) $(\partial T)_P = -(\partial P)_T = 1$
2) $(\partial V)_P = -(\partial P)_V = (\partial V)_P/1 = (\partial V)_P/(\partial T)_P = (\partial V/\partial T)_P = \alpha V$
3) $(\partial S)_P = -(\partial P)_S = (\partial S)_P/(\partial T)_P = C_p/T$
4) $(\partial E)_P = -(\partial P)_E = (\partial E)_P/(\partial T)_P = C_P - P\alpha V$
5) $(\partial H)_P = -(\partial P)_H = C_p$
6) $(\partial S)_T = -(\partial T)_S = \alpha V$
7) $(\partial V)_T = -(\partial T)_V = \kappa V$
8) $(\partial E)_T = -(\partial T)_E = -(\partial E/\partial P)_T = -T(\partial S/\partial P)_T - P\kappa V = T\alpha V - P\kappa V$
9) $(\partial S)_V = -(\partial V)_S = (\partial S/\partial T)_P(-\kappa V) - (\partial S/\partial P)_T(\alpha V) = 1/T[-C_p\kappa V + T(\alpha V)^2]$
10) $(\partial E)_V = (\partial V)_E = T(\partial S)_V = [-C_p\kappa V + T(\alpha V)^2]$
11) $(\partial E)_S = (\partial S)_E = (\partial E/\partial T)_P(\partial S/\partial P)_T = (\partial E)_P(-\partial S)_T = [C_P - P\alpha V](-\alpha V)$
12) $(\partial H)_S = -(\partial S)_H = -C_p\alpha V$

and so on. In some case use of the cyclic relation, $(\partial V/\partial T)_P(\partial T/\partial P)_V(\partial P/\partial V)_T = -1$, can further simplify some of these expressions. Note how the cyclic relation is easily verified with eq. 1.

The 'Magic Square' Solution

Coming back to the 'magic square' Max Born privately used to derive the Maxwell relations, this square has recently been further developed [6-8] to accomplish the Bridgam 'shorthand notation' goal in a much easier way, and without the need to call for the fundamental principles of thermodynamics. Actually, the two methods overlap only partially in their results.

The thermodynamic 'magic square', which formally looks very much like the Aristotelian 'magic square', was developed into two 'magic squares' and used to derive by the aid of characteristic patterns most of the thermodynamic relationships found in a thermodynamics curriculum. The two 'magic squares', known as diagrams for thermodynamic relationships, have been called the E- and the S-diagram as one is an energy-diagram). The arrow direction property states that any operation involving an arrow is positive if it is performed along its direction and negative if it is performed along its anti-direction [6-8].

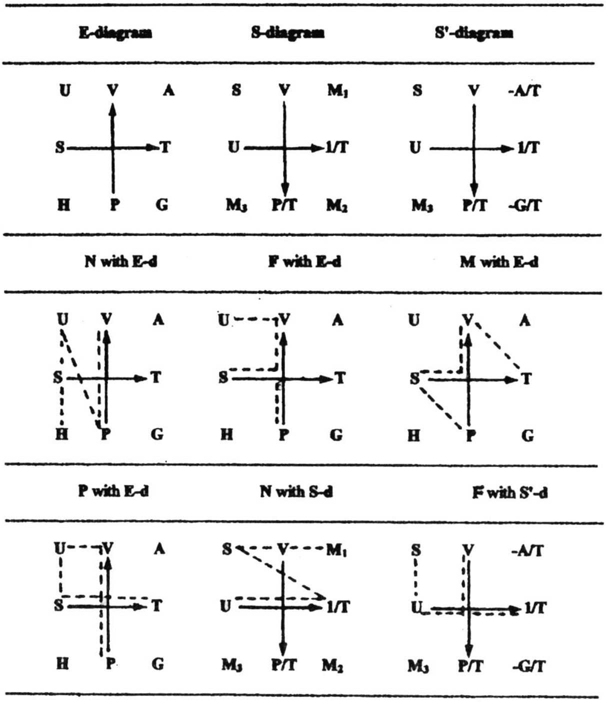


Figure 2. Top: the 'magic' E- and S-diagrams (E-d, S-d) for thermodynamic relationships. The S'-diagram is the explicit form of the S-diagram (see text). *Bottom*: examples of the different uses of N, F, M, P, patterns with the two 'magic' diagrams.

The use of four geometrical 'alphabetical' patterns that trace the shape of a letter will now be shown. These patterns that overlay the E- and S-diagrams (see Figure 2) encompass, in a specific order, the parameters of the diagram, which have to be included in a thermodynamic relation. Their trace indicates the relation among the thermodynamic parameters, with the sign of the parameter being determined by the flow of the trace against the flow of the arrow. Pattern N can be used for the fundamental relations, patterns F for the dimensional diagram, and the other an entropy-dimensional diagram (Figure 2). Our ability to geometrize, allows to recognize some interesting patterns in these two diagrams that can be used to derive, nearly from scratch, the multifarious relationships of thermodynamics of simple PVT systems. Actually, they can also be used for other types of thermodynamic systems [7]. The corners of the E-diagram are occupied by functions from the set of thermodynamic energy functions {U, H, A, G}, while the corners of the S-diagram are occupied by functions from the set of thermodynamic entropy functions {S, M_1, M_2, M_3}. The properties from the set {P, S, T, V} are the main variables of the E-diagram, while properties from the set {U, V, 1/T, P/T} are the main variables of the S-diagram. M_1, M_2, and M_3 are the Massieu functions, after the French mineralogist François-Jacques-Dominique Massieu, who introduced them in 1869, while Gibbs introduced his famous potential in 1875 [9]. The two 'magic squares' allow also to solve specific problems that can be reduced into a series of symmetry operations performed on a diagram by the aid of geometrical patterns. These patterns have normally the form of an alphabetical letter, and their purpose is to show which and how neighbor parameters are related in a thermodynamic relationship.

The 'magic numbers' of the E-diagram (E-d, see Figure 2), are, thus, the energy functions, A, G, H, and U, and the natural variables, P, S, T, and V. For the S-diagram (S-d, see Figure 2) the 'magic numbers' are the entropy functions, M_1, M_2, M_3, and S, and the natural variables, P/T, 1/T, U, and V. The handling of the two sets of 'magic objects' in both 'magic squares' is governed by a series of three properties : (i) the neighborhood property, (ii) the orthogonality property that concerns the diamond set only, and (iii) the arrow direction property. As the relative positions of the two sets of thermodynamic objects in the E- and S-diagrams are uniquely determined by the topology of the diagram, the two diagrams define a '*topological*' space in which only the neighborhood relations are meaningful. The neighborhood property states that the corner parameters are functions of the nearby natural variables. In the E-diagram: A = A(V, T), G = G(T, P), H = H(P, S), and U = U(S, V), while in the S-diagram we have: $M_1 = M_1(V, 1/T)$, $M_2 = M_2(1/T, P/T)$, $M_3 = M_3(P/T, U)$, and S = S(U, V). From these functional relations the total differentials are easily obtained. The orthogonality property states that the natural variables in the diamond structure of the thermodynamic magic squares have to be multiplied only along the same arrow and never between orthogonal arrows. Only in this way it is possible to obtain either an energy-dimensioned term (E-diagram), PV or ST, or an entropy dimensioned term, U/T or PV/T (S-

Energy-function and Entropy-function derivatives, pattern M for the Maxwell relations in the E-diagram, and pattern P for the differential energy or entropy expressions. The N pattern used with the S-diagram allows one to obtain the full thermodynamic expressions for the most important Massieu functions, M_1, and M_2 and that are shown in Figure 2, in the S'-diagram. We will show here only some applications of the E- and S-'magic squares', for those interested to deepen the argument perusal of articles [6-9] is mandatory.

The Fundamental Relations and the N Pattern

The superimposed dashed lines of the N pattern (see Figure 2, second row), starting from the bottom left of letter N draw the following fundamental relation

$$H = U + PV \tag{5}$$

The term PV is imposed by the orthogonality property, which helps, thus, to obtain a homogeneous relation. The sign plus in front of PV is imposed by the arrow direction property, as from P to V the flow of the trace of pattern N parallels the flow of the arrow. Now, either rotating this pattern clockwise (or anti-clockwise) by 90° or reflecting it through an arrow or rotating it by 180° around an arrow, we can obtain all other fundamental relations, i.e, with a clockwise 90° rotation or an anti-clockwise rotation by 90° we have, respectively

$$U = A + ST \tag{6}$$

$$G = H - TS \tag{7}$$

And so on.

The Energy Function Derivatives and the F pattern

The superimposed F pattern, starting from the top left of the F trace (Figure 2, second row, mid pattern), allows to derive the following energy function derivative,

$$(\partial U / \partial V)_S = - P \tag{8}$$

The minus sign arises from the arrow direction property, as the flow of the trace of the long side of F from V to P is against the flow of the arrow. Now, either rotating this pattern clockwise (or anti-clockwise) by 90° or reflecting through an arrow or rotating it 180° around an arrow we can obtain all the other energy function derivatives, i.e, with an anti-clockwise 90° rotation we obtain a relation that is normally considered the thermodynamic definition of the absolute temperature, and which is used to introduced the concept of negative temperatures,

$$(\partial U / \partial S)_V = T \tag{9}$$

Now, reflecting this last picture along the ST axis, the companion of eq, 9 for the thermodynamic definition of the absolute temperature follows

$$(\partial H / \partial S)_P = T \tag{10}$$

The Maxwell Relations and the M pattern

These were the relations that intrigued Max Born [9], and for which he conceived the thermodynamic 'magic square'. The superimposed dashed lines of the slanted M pattern (see Figure 2, second row, right pattern), starting either from P or from T parameters we can derive the following Maxwell relation

$$(\partial P / \partial S)_V = - (\partial T / \partial V)_s \tag{11}$$

The minus sign arises from the arrow direction property, as the flow of the trace of M from T to S is against the flow of the arrow, while the flow of the trace of M from P to V is along the flow of the arrow. Now, rotating this pattern clockwise (or anti-clockwise) by 90° (or 180° around one of the diagonals of the arrow system) we can obtain all the other Maxwell relations, i.e, with a clockwise 90° rotation we obtain

$$(\partial S / \partial V)_T = (\partial P / \partial T)_V \tag{12}$$

And so on, keeping an attentive eye to the signs.

The Differential Energy Expressions and the P Pattern

The superimposed dashed lines of the P-like pattern (see Figure 2, third row, left pattern), starting from the top left corner allow us to draw the following differential energy expression

$$dU = dS{\cdot}T - dV{\cdot}P \qquad (13)$$

Upon rearranging we obtain the well-known differential relation: dU = SdT - PdV. The minus sign originates from the arrow direction property, as the flow of the trace of P from V to P is against the flow of the arrow. Now, either rotating this pattern clockwise (or anti-clockwise) by 90° or rotating by 180° around an arrow, or reflecting it through an arrow we can obtain all the other differential relations, i.e, with a clockwise 90° rotation we obtain

$$dA = - dT{\cdot}S - dV{\cdot}P \qquad (14)$$

upon rearranging we have: dA = -S dT - PdV. With an inversion of pattern P through the center of the diamond we have

$$dG = - dT{\cdot}S + dP{\cdot}V \qquad (15)$$

and upon rearranging we have: dG = -S dT + VdP. And so on.

The Massieu Functions

The Fundamental Massieu Relations and the N Pattern

Before starting the procedure we underline that the vertical arrow in the S-diagram is now pointing to the bottom of the diagram. The N pattern used as shown in see Figure 2, third row (mid pattern, N with S-d), allows us to derive the explicit thermodynamic expression for the first Massieu function

$$M_1 = S - (1/T)U \quad (16)$$

The minus sign originates from the arrow direction property, as the flow of the trace of N from 1/T from to U is against the flow of the arrow. Rearranging we obtain: $M_1 = (TS - U)/T$, which, thanks to an N relation of the E-diagram, $A = U - TS$ (see eq. 6), equals $-A/T$, that is, $M_1 = -A/T$. This explicit expression for M_1 has been introduced into the S'-diagram (see Figure 2 first row, last diagram). Now, rotating this N pattern around the S-diagram (or reflecting through a diamond axis) we can obtain the other expressions for M_2, M_3, and S, i.e.,

$$M_2 = M_3 - (1/T)U \quad (17)$$

$$M_3 = S - (P/T)V \quad (18)$$

$$S = M_1 + U(1/T) \quad (19)$$

Inserting eq. 18 into eq. 17 we have

$$M_2 = S - (P/T)V - (1/T)U \quad (20)$$

This last equation can be rearranged into: $M_2 = S - (PV + U)/T$, now, two N relations of the E-diagram, $H = U+PV$ (eq. 5), and $G = H - TS$ (eq. 7) help us to obtain,

$$M_2 = S - H/T = -G/T \quad (22)$$

The found explicit expression for M_2 is the well-known Planck function and has been inserted into the S'-diagram (see Figure 2, third diagram). The M_3 function, which has no practical uses in thermodynamics has been left as it is in the S'-diagram, but its explicit relationship can also be 'discovered' in the same way with pattern N.

The Entropy Function Derivatives and the F pattern

The F pattern (Figure 2, third row, F with S'-d) will now be used with the S-diagram to derive the other relationship, which can also be used to define the thermodynamic concept of absolute temperature, i.e,

$$(\partial S/\partial U)_V = 1/T \quad (21)$$

Conclusion

'Magic squares', born more than two thousand years ago in China not only constitute a strange curiosity for historians of science but they represent a nice formal solution to many scientific problems in some domains of science. In this work we have traced the strange path that goes from an intriguing Chinese 'magic graph' endowed with a consistent set of numerical properties, to a present thermodynamic 'magic square' endowed of a rich set of non-metric properties. These properties, which are based on the topology of two thermodynamic squares, the E-diagram and the S-diagram, allow us to derive and check an enormous set of thermodynamic relationships in a total automatic way [7, 8].

The history of 'magic tools' has recently been enriched with the discovery of a 'magic hexagon', i.e, a complete graph on six points, which has been suggested as a graphical representation of the Dirac algebra in quantum mechanics (QM). This 'magic hexagon' showing all commutation and anti commutation relations helps to analyze some QM theorems [22]. Actually, strange exagonal patterns emerge if the strangeness of the eight spin 1/2 baryons is plotted against their charge quantum number: six of the eight baryons form a hexagon with the two remaining baryons at its center. The same is valid for the nine spin zero mesons, here the three remaining mesons are at the center of the hexagon. The quarks composition of the eight spin 1/2 baryons (each baryon is a combination of three quarks), as well as the quark composition of the nine spin zero mesons (mesons are quark-antiquark pairs) show the same hexagonal pattern [23].

Let us conclude with a quotation by Cajori [24] that fits the purpose of the 'magic square' to solve complicated problems by a minimum mental effort: *if it is the purpose of mathematics to resolve complicated problems by a minimum mental effort, then this device takes high rank.*

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