
Questions and Answers

Statistical Determination of Absolute Zero Temperature

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It is shown that the position of the absolute zero of temperature relative to the Celsius scale can be determined in a number of ways using a statistical analysis of complex physical phenomena.

KEY WORDS: Temperature scales; absolute zero; statistical inference; third law of thermodynamics.

1. INTRODUCTION

The power of statistical science, in our opinion, is not yet fully exploited in physics; at least, not as much as in other fields such as economics or psychology, for example. The above statement sounds preposterous in the *Journal of Statistical Physics*, but a little reflection will show that indeed statistics is used by the physicist in a more restricted sense than by the pure statistician.

Take the statistical analysis of a physical experiment. When a physicist plots a quantity y versus a quantity x , he always implies that there is a "true" functional dependence of y on x [a "law" of physics of the form $y = y(x)$]. When his experimental points (x_k, y_k) do not fit a curve, he will blame the failure on the experimental "errors." If he does not succeed in fitting a curve, even by improving on his experimental techniques, he will probably say that there is no physical law connecting the two

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quantities and leave the matter as not worth further investigation. Yet there are statistical relations that do not imply a functional dependence and are standard topics of investigation for statisticians, such as height versus weight in conscripts and wheat yield versus rainfall. Admittedly, the latter types of statistical investigation have also found a limited place in physics, in so-called statistical mechanics. However, it seems to us they have been confined within a too narrow range.

To make our discussion more precise, we shall consider only a particular case in this paper: the determination of the absolute zero of temperature by a statistical analysis of phenomena for which no precise physical laws exist, but only statistical dependences in the above sense.

In short, the basic idea is as follows. We know that nature has a preferred temperature scale—the absolute thermodynamic scale—with a privileged point $T = 0$. The discovery of such a temperature has been one of the milestones of thermodynamics and the position of $T = 0$ relative to the Celsius scale can now be determined using scores of different physical laws. Can it be determined—without invoking any particular law—with an analysis of statistically correlated phenomena? We will show that this is indeed possible in quite a number of surprising ways, from a statistical examination of the melting and boiling temperatures of various compounds or from an analysis of the air temperatures in a desert.

2. THE CORRELATION BETWEEN BOILING AND MELTING TEMPERATURES IN DIFFERENT COMPOUNDS

A cursory inspection of a table of physical constants shows that the boiling point t_b of a compound (at normal atmospheric pressure) is correlated with the melting point t_m of the same compound. The higher t_m , the higher t_b . Naturally, it is a very crude relation, full of “anomalies,” as a physicist would probably put it; one can easily find compounds melting at the same temperature which have very different boiling temperatures and vice versa. Even if we had a completely satisfactory theory of the solid and liquid state, allowing us to derive the melting and boiling temperatures of a given compound from basic principles, it is out of the question to think of a physical law connecting t_b and t_m for *all* compounds. In short, we have just the type of statistical dependence, without a functional dependence, we mentioned in the introduction.

Let us try to fit all the “experimental points of nature” in a t_b versus t_m diagram with a straight line. According to statistics, this is the *orthogonal mean-square regression line* that puts both variables on equal footing (i.e., the major axis of the ellipse of inertia of the distribution).⁽¹⁾

Using all the inorganic and organic compounds listed in the L.B.-tables⁽²⁾ for which both melting and boiling temperatures were given at normal atmospheric pressure (a total of 1479 substances, including the elements),² we found for such a line the equation

$$(t_b - 350) = 1.786(t_m - 75) \quad (1)$$

² We excluded only deuterated compounds such as CD_4 , which seemed to be merely duplications of the ordinary compounds. Including them would have left the result unchanged.

in the Celsius scale. If we like to elaborate on the correlation between t_b and t_m , we might think that nature is experimenting with various compounds, making “errors,” “poor measurements,” trying to fit the “true law” given by Eq. (1).³

Now, if nature has a preference for the absolute temperature scale, this fact should show up in Eq. (1), which in a way summarizes all (or at least is a good sampling of) the experiments of nature. The only way this can happen is for Eq. (1) to take a particularly simple form when temperatures are expressed in the absolute scale T . The only simplification we can think of is for Eq. (1) to be written in the form

$$T_b = \alpha T_m, \tag{2}$$

i.e., the line should pass through the origin in the reference system of absolute temperatures. The angular coefficient α must still be equal to 1.786, if we use the same unit interval for the definition of one degree in both the centigrade and absolute scales. It is then an easy matter to find A in the relation

$$t = T + A \tag{3}$$

It is the point (A, A) where the line (1) crosses the bisector

$$t_b = t_m \tag{4}$$

in the (t_b, t_m) plane. The result is

$$A = -[350 - (1.786)(75)]/0.786 = -275^\circ\text{C} \tag{5}$$

Of course, this remarkable result might be considered nothing more than a lucky coincidence. Therefore, let us explore the question a little further.

Our basic assumption—the correlation line should show up the preference of nature for the absolute temperature scale—can be carried over unchanged for any other pair of correlated temperatures. Therefore, we should be able to arrive at the same result using other pairs of correlated temperatures: the critical temperature versus the melting temperature, the critical temperature versus the boiling temperature, etc.

As a check, we took all the compounds (206 in all) for which we had the critical temperature t_c , the melting point t_m , and the boiling point t_p .⁴ Repeating the same calculations as before, we got

$$\begin{aligned} A &= -266^\circ\text{C}^5 && \text{for the pair } (t_b, t_m) \\ A &= -276^\circ\text{C} && (t_c, t_m) \\ A &= -361^\circ\text{C} && (t_c, t_b) \end{aligned}$$

We can go a step further. We can plot t_m , t_b , and t_c in a three-dimensional diagram and find the best linear fit in three dimensions (the major axis of the ellipsoid of

³ Of course, we are not so philosophically naive; the above statement should be taken with a grain of salt.

⁴ The data are taken from Ref. 3.

⁵ This result is different from the one given above because here we only had 206 compounds instead of 1479.

inertia of the distribution). Repeating the usual argument, we should then look for a translation (3) on all the three temperature axes that reduces the correlation line to the form

$$T_c = \alpha T_m = \beta T_b \quad (6)$$

The two equations (6) cannot be solved for one unknown A , i.e., we can only look for the point (A, A, A) on the line

$$t_c = t_m = t_b \quad (7)$$

that gives the closest approach to the three-dimensional correlation line. The result is $A = -280^\circ\text{C}$. The distance of closest approach turns out to be $d = 22^\circ\text{C}$. This gives a measure of the error in A , so that we can write

$$A = -280 \pm 22^\circ\text{C} \quad (8)$$

We do not want to bore the reader with other examples. It suffices to say that we found for A values of the same order, whatever pair of correlated temperatures we tried (for example, the temperature at which the vapor pressure of a compound is p versus the temperature at which it is P , and the like). We found apparently only one exception, which we will discuss in detail in the next section.

It seems, therefore, that by statistically analyzing complex, temperature-dependent phenomena, the information related to the preference of nature for the absolute temperature scale is not destroyed by the averaging process.

3. CORRELATION OF METEOROLOGICAL TEMPERATURES

Can we think of a day in Genoa with its minimum and maximum temperatures as something analogous to a compound with its two characteristic (melting and boiling) temperatures? Those temperatures are obviously correlated (high in summer and low in winter). More for fun than out of conviction, we tried with the minimum and maximum daily temperatures in Genoa for a year (1966). We got $A = -36^\circ\text{C}$.

The reason for the discrepancy is apparent. Whereas in the former cases there is one privileged temperature $T = 0$, in this case there are *two* different privileged temperatures: besides the *physical* ($T = 0$), there is a *geophysical* temperature (maybe $t = 0^\circ\text{C}$, the melting point of ice), that tells the geophysical relevance of water. No wonder the correlation line passes somewhat between those two points. But then, by the same token, in other places, we should find for A a value approaching one or the other privileged temperature, depending on the relevance of water in that place. We have not been able to collect as much data as we would have liked to (and even if we had, the amount of work necessary to punch cards for the computer is beyond the facilities available to us). We only list in Table I the results of the few cases we were able to get. Maybe some of our readers can work out a more meaningful statistics.

The scant data of Table I seem to confirm our conjecture. Our surmise is that using data from a more arid place than Tucson, Arizona (maybe the Sahara or the Gobi desert) one should find an even better approximation to the absolute zero of temperature.

Table I

Place ^a	Year	A values, °C
Dili (Timor)	1968	+50
Mindelo (Cabo Verde)	1961	+6
S. Martial (Haiti)	1960	+14
Mahon (Balears)	1962	-20
Sevilla (Spain)	1962	-10
Ksara (Lebanon)	1967	-14
Yuma (Arizona)	1969	-190
Tucson (Arizona)	1969	-202

^a The first four places listed are islands.

4. CONCLUSIONS

The methods for the determination of the absolute zero of temperature discussed in this paper are obviously not meant to compete with any of the far more precise standard procedures. We only wanted to show that a more open-minded approach to the investigation of physical laws might prove rewarding. It is amusing to think that a statistician, without the slightest ideas of physical laws, could have arrived in many different ways at the conclusion that "something peculiar seems to occur at about $t \sim -280^\circ\text{C}$." We are sure that with a little ingenuity, one can get similar relevant information in other fields of physics, which could perhaps vastly expand the present limited domain of statistical mechanics.

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