

Entropy

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MANY of the important ideas of physics are of such recent birth that if they still seem hard to grasp, it may be contended that the world has not yet had the time to assimilate them. Of entropy this cannot be said; with its centenary almost upon us, entropy is ancient compared with most of the concepts which baffle the student today. Yet an aura of mystery seems to envelop it still, and two other things inseparably joined to it: the scale of temperature called absolute, and the Second Law of Thermodynamics. One is driven to wonder why the three of them resist the understanding so tenaciously, and certain reasons are not hard to find. Thus, to speak of the three as "joined together" is too weak, for it implies that they can at least be taken in a certain order for didactic purposes, the student ascending from the one to the next and finally to the last. Actually they are much too tightly interlocked for this, a sort of trinity one and indivisible, which must be apprehended as a whole if ever to be properly grasped at all. Again, the Second Law has been expressed in many different ways, and it is one of the oddest things in science to see how various authorities can claim that the law is obeyed absolutely without exception, while they themselves cannot agree how to state it. A further cause of trouble lies in the unlucky boundary between chemistry and physics, which nowhere harms these sciences more than in the study of entropy. Like the worst of the old-fashioned boundaries of Europe, it wanders capriciously across the natural lines of intercourse and trade, cutting off the traditional chemist from the origin and development of some of his most valuable ideas, cutting off the traditional physicist from some of the finest verifications of the thought of his fore-runners. It will be the principal object of this paper to dwell on these verifications, abolishing the barrier so far as may be feasible.

First to illustrate how the three ideas are tangled up together, I give one of the most useful of the definitions of entropy: *when a system passes in a reversible way from one to another state, at a constant absolute temperature T , its change of entropy ΔS is equal to the heat Q which it absorbs, divided by T .* That both the entropy and the absolute temperature have slipped into this definition is all too obvious; as for the Second Law, it lurks underneath the phrase "in a reversible way." Quite evidently we are invited to master all the three in a single mental operation, but quite as evidently this is impossible. A breach must somehow be made in this hard and unified surface,

and the best of scaling-ladders appears to be the ideal gas, as everybody has used it for the purpose.

We therefore receive the definition of the "ideal gas": a substance whereof (a) the temperature remains unchanged when the gas is given and seizes the chance of expanding without any hindrance into a vacuous space; and (b) the pressure varies inversely as the volume, so long as the temperature remains unchanged. Now rather than being an aid to enter the citadel, this definition appears to presume that we are in the citadel already, since the word of "temperature" is all too prominent in it. But the word comes up only in the phrase "... temperature remains unchanged ..."; so nothing more is implied, than that the onlooker knows how to recognize whether temperature is changing or staying the same. This ability can be his, whether or not he knows about the scale called absolute; and so the definition implies nothing about the scale.

The definition would be an idle collection of words, were there not actual gases conforming to it so nearly, that at least for a time they may safely be taken to conform to it exactly. All gases in fact approach conformity, as the density lessens; and with helium and hydrogen especially, the approach is already close while the density is still so high that there is no trouble at all in using them as thermometers. Now, to use an ideal gas as a thermometer means simply this: P being the pressure of the gas and V its volume and n the quantity of the gas measured in moles, there is the equation,

$$PV = nRT \quad (1)$$

which is a mixture of a new definition and a theorem. The part which is definition is, that the temperature called absolute is taken to be proportional to the product PV . The part which is theorem is, that if at the same temperature we compare the product PV for equal numbers of moles of various gases, its value is the same. What is denoted by R in equation (1) is a universal constant. Its value is 1.985 in the customary units, which are calories per degree per mole. Since now the degree of temperature has appeared in this discourse, I recall that its value is fixed by the convention that there are one hundred degrees from the freezing to the boiling point of water; but on this I need not dwell.

It is tacitly assumed that nothing in this definition will ever clash with the threefold simultaneous definition of temperature and entropy and Second Law, should we ever arrive at it. Taking this for granted, and taking advantage of the breach which has thus been made in the formerly impenetrable surface of our definition of entropy, we now attack the concepts of "state" and "reversible way."

The usual way of dealing with "state" is to say that it is determined completely by any two of the three variables P , V , and T , which are inter-

connected among themselves by what is called an "equation of state." This takes for granted that one knows what kind of substance one is speaking of, how many moles there are of it, and which phase it is in; for the statement is valid not only for gases but also for liquids, and even (under certain restrictions) for solids. If two or three phases are coexisting, precautions must be taken. The statement is not valid for mixtures of substances which differ; but there is doubt as to just how much it takes to constitute a difference, and isotopes of a single element are usually considered to be the same.

Now let us envisage two states which differ in temperature but are the same in pressure. P is to stand for the common value of pressure, T_0 for the lower and T_1 for the higher of the temperatures. For the utmost in simplicity at the beginning, the substance shall be an ideal gas, and moreover a gas of which the specific heats do not depend upon the temperature; any noble gas under ordinary conditions approaches very closely to these stipulations.

One may operate the transition from (P, T_0) to (P, T_1) in the manner which follows: Let the gas be heated from T_0 to T_1 while the volume of its container remains the same. Its pressure will have gone up meanwhile; let this situation be remedied by piercing a hole through the container wall, into an evacuated chamber prepared in advance of just the right dimensions, so that after the "free expansion" the pressure of the gas will be down again to P . The temperature will still be T_1 , for that is one of the qualities of the ideal gas.

Or one may operate the transition in the manner which follows: Let the container be made in advance with a movable wall, say a piston-head against which an outer pressure P —it might be that of the atmosphere—is steadily pressing. Let the gas be gradually heated: as its temperature rises, the piston-head glides gradually outward, increasing the volume of the container at such a rate that the pressure of the gas always remains the same and equal to P . The process is to be stopped when the temperature reaches T_1 .

These, then, are two very different ways of carrying through the transition; and the reason for bringing them in is to elucidate the words "in a reversible way" which occur in the phrase defining entropy. The former way includes a process which is spontaneous, rapid, turbulent, explosive; nothing can inhibit it when the piercing of the hole creates the opportunity. The latter way is gradual, languid, crawling, always on the verge of stopping, would instantly stop if the inflow of heat should cease, would reverse its trend if the inflow should be turned into outflow. The former way includes a process during which the pressure of the gas is ill-defined or not defined at all, for the gas is spurting through the hole and reverberating in the chamber

formerly empty. During the entire latter process, if it be gradual enough, the pressure of the gas is definite, and related to V and T by the equation (1). The former is an irreversible way of effecting the transition. The latter is *the reversible way* of effecting the transition.

As the heat flows into the gas, its entropy mounts up. Since the temperature is meanwhile changing, we must mentally subdivide the incoming heat into dribblets dQ , during the inflow of each of which T remains about the same. The corresponding dribblets of energy are given by dQ/T , the total change in entropy due to inflow of heat is given by $\int dQ/T$ integrated from beginning to end of the inflow.¹ By the former way the integral is $\int (C_v/T)dT$ or $C_v \ln(T_1/T_0)$, by the latter way the integral is $\int (C_p/T)dT$ or $C_p \ln(T_1/T_0)$. The two are not the same. Now we see why the phrase "in a reversible way" was necessary in the definition of change-of-entropy. But for that phrase or something similar, we should now have no definition. But having accepted the phrase, we are invited and required to write,

$$\Delta S = \int (C_p/T) dT \quad (2)$$

for all transitions of a single substance within a single phase; ΔS signifying the change of entropy, and the use of C_p implying that the conditions are those under which specific heat at constant pressure is properly measured: the pressure of the substance being definite, nothing turbulent or gusty or explosive happening within the substance, and an equal pressure bearing down upon it from the outer world.

We have now the necessary and complete statement for the variation of entropy with temperature, pressure remaining the same; but it has to be supplemented with a statement for the dependence of entropy on pressure, T remaining the same. For this and other purposes, let us return to the irreversible passage between (P, T_0) and (P, T_1) —the passage, rather, of which one stage is reversible but the other not. During the reversible stage, the gain of entropy is $\int (C_v/T)dT$. This falls short of the gain of entropy incurred along the other route as given by (2). However the other route leads reversibly all the way to the goal, while the reversible part of this one brings us only a part of the way, leaving us with the irreversible expansion still before us. By assuming that the remainder of the total gain of entropy demanded by (2) is made up during the irreversible expansion, we rescue the concept of entropy. Now to save and establish the concept

¹ It is often said or implied that this formula should not be used unless the process is fully reversible, in the sense that the inflow of heat occurs from a reservoir of temperature identical with that of the gas. As no such precaution is taken when specific heats are measured, and as measurements of specific heat are commonly used for establishing values of entropy, I assume that the limitation is needless.

of entropy, to make it a definite property of the state of a substance, is one of the offices of the Second Law.

It is therefore a part and a consequence of the Second Law to affirm that when an ideal gas undergoes a free expansion, it experiences a gain of entropy despite the fact that it receives no heat from the world without! Nor is the affirmation confined to ideal gases; it would be true of any substance, though in general a free expansion would be attended with a change in temperature. Nothing, therefore, could be more wrong than to repeat our first definition of change-of-entropy with the words "in a reversible way" left out.

One now begins to see why the concept of entropy is so much harder to receive than that of energy. Every scientist is accustomed by now to the "conservation" of energy: whereby it is meant that if the energy of a system rises or falls by any amount, it is because there has been an inflow or an efflux of just that amount from or into the outer world. Nothing of the sort can be said of entropy, of which we have just seen that it may vary even within a system which is having no transactions at all with the outer world. One may not speak of the conservation of entropy excepting under the sharp and severe restriction that all of the processes in the system *and* in the outside world are reversible: and "reversible" must be used in the full sense adumbrated in a previous footnote, whereby no transfer of heat is reversible unless the body whence it comes and the body to which it goes are of identical temperature. Yet nothing of all this contradicts the assertion that entropy and energy are, both of them, uniquely determined functions of the state of a system—functions, therefore, of any two of the three variables P and V and T , for substances of a single kind in a single phase.

Since the equating of entropy-change to inflow of heat divided by temperature is something that positively must not be done for an irreversible process, we must seek other ways to assess it.

One such way has already been stated. If it is possible to start from a particular state, and thence to arrive by reversible ways at both the beginning and the end of the irreversible process in question, all the necessary knowledge is at hand; for now by integrating dQ/T along the two ways we find two quantities, of which the difference is the entropy-change desired.

Applied in the special case which we have been considering, this method has given

$$\Delta S = (C_p - C_v) \ln (T_1/T_0) \quad (3)$$

not, however, a useful expression as yet, since it contains a quantity (T_0) which does not figure at all in the irreversible process in question—a process which, I recall, is the free expansion of one mole of ideal gas, at a constant temperature T_1 , from a higher pressure and lower volume which we will denote by P' and V' , to a lower pressure and a higher volume which we will

denote by P and V . Remembering (1) the equation of state of the ideal gas, and applying it to the reversible heating at constant volume which preceded this expansion, we find

$$T_1/T_0 = P'/P \quad (4)$$

and so,

$$\Delta S = (C_p - C_v) \ln (P'/P) \quad (5)$$

for the entropy-change incurred when one mole of ideal gas expands at uniform temperature so that its pressure falls from P' to P . I do not have to state the temperature, since it has vanished from the equation. I do not have to say that the expansion is irreversible, for if there be such a thing as entropy at all, its alteration depends only upon its values in the initial and in the final state, and not on the manner in which the system has made the passage from initial to final. I ought, however, to recall that we are still supposing a gas of which the specific heats do not depend upon temperature, nor in fact upon any variable whatsoever.

Now we have an expression—equation (5)—for the way in which entropy changes with pressure at constant temperature, and another—equation (2)—for the way in which entropy changes with temperature at constant pressure. We may combine them to get the change of entropy occurring when the gas proceeds, by whatever route, from an initial state (P_1, T_1) to a final state (P_2, T_2) . This is,

$$S_2 - S_1 = C_p \ln(T_2/T_1) - (C_p - C_v) \ln(P_2/P_1) \quad (6)$$

which, by stripping off the subscripts 2, and gathering into one term I all of the terms containing the subscripts 1, may be written,

$$S = C_p \ln T - (C_p - C_v) \ln P + I \quad (7)$$

the expression, for a gas of the special type stated, of entropy as a function of absolute temperature and of pressure. The quantity I is an "additive constant" which will turn out to be one of the major topics of this paper.

All this way we have come without invoking the First Law of thermodynamics, and we might even go further without its aid! But there is no point in deferring it longer, and I wish to be able to convert (7) into a more familiar form by replacing $(C_p - C_v)$ with the constant R of the equation-of-state of the ideal gas. To do this I return to the irreversible process which has so long engaged our attention; the free expansion of the gas from the higher pressure P' to the lower pressure P , its temperature remaining the same. I seek a reversible way of conducting the expansion from the same beginning to the same ending under the same condition of steady temperature. A reversible way of going between the extremes we have

indeed already found, but it involves a retracing of our steps: the cooling of the gas to a lower temperature at a constant volume, followed by the heating of the gas to the original temperature at the constant pressure. We wish a forward-going reversible way, and such a one can be found. It is necessary to have the container built with a frictionless piston-head for one wall, and to bear down upon this from without with a pressure always nicely calculated to be equal to the internal pressure of the gas. If under this condition the piston-head is gliding slowly outward it will continue so to glide, and the gas will expand in the gradual, languid, crawling manner, with its internal pressure always definite—the manner which we call “reversible.” All that is now required is to know the amount of heat which enters the gas during this process, so that we may divide it by T and so assess the entropy-change. It is from the First Law that we get this information.

The First Law is to be spoken in the form

$$\text{energy-gain} = \text{“heat in”} \text{ less “work out”}$$

and written in the form

$$\Delta U = \Delta Q - \Delta W \quad (8)$$

the symbols fitting the words in the way which is obvious.

For an ideal gas, the energy U is independent of pressure or volume, depending on the temperature alone. The reader may or may not take this as a matter of course, but it will be proved later on. We are considering an isothermal expansion, and therefore ΔU is zero, and the problem of evaluating ΔQ is that of evaluating ΔW . Now the “work out”—the work done by the gas upon the outer world—is equal to the pressure bearing down upon the piston-head from the outer world, multiplied by the area of the piston-head and the distance through which it advances. The last two factors multiplied together give the gain in volume of the gas, ΔV ; and without a moment’s hesitation one usually puts for the first factor the symbol P signifying the pressure of the gas. However, it is wise to hesitate just long enough to realize that by so doing one assumes the *reversible* expansion with all the attributes set forth above. For an irreversible expansion ΔW would not be equal to $P\Delta V$, but less. But assuming the reversible expansion, and remembering that P is not independent of volume as in these last few lines I have tacitly assumed, we find

$$\begin{aligned} \Delta W &= \int P dV = RT \int (1/V) dV \\ &= RT \ln (V/V') = RT \ln (P'/P) \end{aligned} \quad (9)$$

the unprimed symbols referring to the final state of the expanding gas and the primed symbols to the initial state. Now identifying ΔW with ΔQ , and dividing it by T to get the change-of-entropy, we have for the very quantity ΔS which figured in equation (5) a second expression, *viz.*

$$\Delta S = R \ln(P'/P) \quad (10)$$

where now R stands in place of $(C_p - C_v)$. We make the substitution into (7), and arrive at our next-to-final form for the entropy of the ideal gas of constant specific heats:

$$S = C_p \ln T - R \ln P + I \text{ (one mole)} \quad (11)$$

I pause to mention that since for any gas PV/T is measurable and so is also $(C_p - C_v)$, the rightness of our assumptions may be tested by ascertaining whether for gases nearly ideal, the one—which for an ideal gas is R —and the other are nearly equal. This is so; and if we wish to pick out a special one among the assumptions for which this shall constitute a special test, then we may set down as having been particularly proved the assertion, that the energy of an ideal gas depends upon its temperature alone and not upon its pressure nor its volume.

For quite some time I have been referring to a single mole of the gas in question; but for an odd and probably an unexpected reason, it is going to be desirable to make an explicit broadening of these equations to the general case of any number n of moles. The broadening required for (11) is so simple and trite as to seem not worth the doing: we have simply to multiply every term of (11) by n , and so obtain

$$S = nC_p \ln T - nR \ln P + nI \text{ (} n \text{ moles)} \quad (12)$$

But now let us translate this into an expression for S as a function of volume and temperature, by use of the fact that P is nRT/V , and the further fact that R is $C_p - C_v$. We come upon the astonishing equation,

$$S = nC_v \ln T + nR \ln V - nR \ln(nR) + nI \quad (13)$$

astonishing because the terms to the right of $nR \ln V$ are not reducible to n multiplied into a constant, but involve a more intricate function of n . Perhaps, after all, we ought not to have taken the simple recourse of broadening (12) by multiplying n into every term of (11) including the last one? Actually it is quite all right; the additive constant in (12) is truly proportionate to the number n of moles; that in (13) is the more intricate function of n which we have just derived.

In Fig. 1 there is shown a "phase-diagram" appropriate to a substance of a single kind, capable of existing as a gas and as a liquid and as a solid. Pressure and temperature are the coordinates along the vertical and hori-

zontal axes, but no coordinate-scales are shown, and no attempt has been made to shape the curves in exactly the manner correct for any particular substance, since all that matters here is the general idea. Envisage any point (P, T) in the area "gas," lying just off the curve which separates that area and the other one marked "solid." This is the point—I will call it the "point of interest"—for which we are to obtain two expressions for entropy S arising from different sources, and find an important result by comparing the two so obtained.

One of the two is of course the right-hand member of (12). It may create surprise that one should be treating the gas as ideal, under conditions where the slightest fall in temperature or rise in pressure would con-

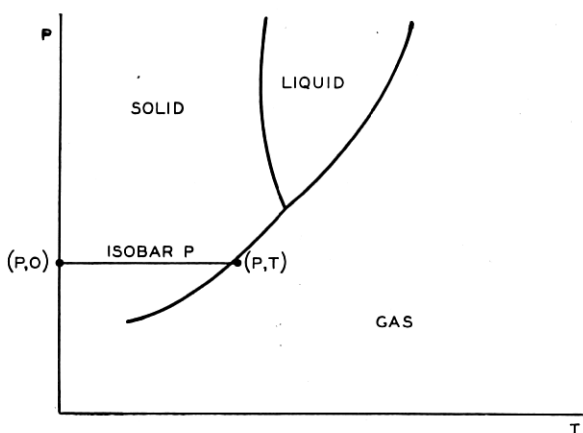


Fig. 1

dense it. The approximation, however, may still be a good one, and if it is not close, the equation of state of the actual gas may be used in place of (1).

To form the other expression, we commence at the point $(P, 0)$ where the isobar P which traverses the point of interest reaches the vertical axis, and call the entropy there by the symbol $S(P, 0)$. We proceed along the isobar toward the point of interest, building up the integral $\int (C_p/T)dT$; since we remain in the area called "solid," it is C_p of the solid which concerns us, and we may mark it so. Just before the isobar passes over the curve dividing solid from gas, the entropy arrives at the value

$$S(P, 0) + \int_0^T (C_p^{sol}/T) dT$$

but this is not yet the value at the point of interest, for the "divide" is yet to be crossed. At the crossing of the divide a certain amount of heat is

absorbed: denote it by L for one mole. If the crossing of the divide is a reversible process, the entropy of the substance goes up by L/T as it turns from solid to gas.

Is the crossing of the divide a reversible process? It is indeed, and that is why phase-diagrams are constructed. Think of the substance enclosed in a container with frictionless piston-head, equal pressures P bearing upon the piston from the world without and from the substance within, and the whole affair at temperature T . If the point defined by P and T lies exactly on one of the curves which partition the diagram off, then the substance within the container may be a mixture of the two adjoining phases in any ratio imaginable. If the piston-head is gliding slowly inward it continues so to glide, P and T remaining steadily the same while all that there is of the phase of greater specific volume² is converted gradually into the other. If the piston-head is gliding slowly outward it continues so to glide, P and T remaining constant while the latter phase is converted into the former. All of the attributes of the reversible process are here: gradualness, lack of turbulence and of explosiveness, willingness to go in either sense, willingness to stand indefinitely still at any partway stage. For ease of formulation it is the prince of reversible processes, since P and T are both unchanging while it is going on.³

Accepting then the crossing of the divide as a reversible process, we have our second expression for the entropy at the point of interest:

$$S(P, T) = S(P, 0) + \int_0^T (C_p^{sol}/T) dT + L/T \quad (14)$$

I pause to quiet the fear that the expression here written down is necessarily infinite, because of T standing in the denominator of the integrand on the right! It is a fact of experience that as T approaches absolute zero, C_p approaches zero for all solids, and with such rapidity that (if extrapolation is safe) the integrand tends to zero and not to infinity. Now comes the climax, which consists in equating the right-hand members of (12) and (14). Referring to a single mole of the substance, and rearranging the terms, we find:

² Volume per unit mass.

³ Irreversible transitions from "supercooled" liquid to solid may occur. In such a case the area called "liquid" may be regarded as spreading somewhat over the divide and overlapping a portion of the area called "solid." The values of P and T for any point in this region of overlapping may characterize either a solid or a liquid, though what is called a "liquid" for this purpose may be so stiff and tough as to deserve and bear the name of "glass." If the solid and the liquid are brought into contact the latter may pass into the former (but never the former into the latter) in a manner so nearly explosive as to be clearly not reversible. I should be less than frank were I to imply that this is always so. With the transition from "supersaturated gas" to liquid, the irreversibility is manifest.

$$I - S(P, 0) = R \ln P - C_p^{gas} \ln T + \int (C_p^{sol}/T) dT + L/T \quad (15)$$

All of the terms on the right are measurable quantities, excepting that C_p^{sol} cannot be followed clear down to the absolute zero, so that the piece of the integral extending from zero up to a few degrees absolute must be guessed. Now at the bottom of the accessible temperature-range C_p is already very small, and in most cases the curve of C_p versus T seems to be heading very smoothly toward zero, so that the uncertainty is probably slight. Surprises in the unreachable range are, however, not inconceivable.

Everyone familiar with entropy will have known in advance, and on reading equations (12) and (14) will have remembered, that the additive constants I and $S(P, 0)$ are beyond the reach of all experiment, be it physical or be it chemical. No way can be devised of measuring them, for in chemistry or in physics it is never the entropy of a system in any one state which is measured, but only the difference of the entropies in two different states, and the additive constant is cancelled in the subtraction. So far as (12) by itself or (14) by itself is concerned, each constant is but a vain appendage, and to develop a theoretical value of either would be reasoning in a void. In spite of all this, the difference between I and $S(P, 0)$ is within the reach of experiment. This permits of one, or two, or even of all three of the following situations:

(a) If there is a plausible theory of entropy which leads to a value for I , experiment will fix a value for $S(P, 0)$ corresponding to that theory.

(b) If there is a plausible theory of entropy which leads to a value for $S(P, 0)$, experiment will fix a value for I corresponding to that theory.

(c) If there is a theory which leads to a value for $S(P, 0)$, and there is another and independent theory which leads to a value for I , then experiment can tell whether the two are compatible.

The actual situation is most nearly like the last of these three; and from this viewpoint I will describe it.

Before going on to the theories of I and of $S(P, 0)$ I point out that (15) is the equation of the vapor-pressure curve; for P and T occur in it as variables, and it refers explicitly to such paired values of P and T as correspond to points lying on the divide between solid and gas, and P for any such point is called the vapor-pressure of the substance for the temperature corresponding. Measurements of vapor-pressure are therefore the ones which are called to decide on these questions—measurements of vapor-pressure and of specific heat, and of the heat of vaporization. The last-named, the quantity L , need be measured at a single temperature only, for there is a formula which gives its value at any temperature in terms of its value at any other temperature and the specific heats over the range between.

This is often incorporated into (15), and alters its aspect; but until page 71 I will pass over this detail. If the point (P, T) lies beside the liquid-gas divide, the isobar to which (14) refers will cut both this and the solid-liquid divide, and traverse the liquid region. Extra terms will then appear in (14) and in (15), but I leave it to the student to divine them.

THE THEORY OF THE CONSTANT S_0

The theory of the constant S_0 is easy to state, provided that no objection is raised to having it stated in a manner rather too drastic at first, and waiting for the necessary reservations to be added later.

The constant S_0 —the entropy at the absolute zero—is taken to be zero for every substance of a single kind.

This is a way of putting, and the strongest possible way of putting, what is known as "Nernst's Law" or "Nernst's Heat Theorem" or even "the Third Law of thermodynamics." Originally expressed in a much milder form nearly forty years ago, it rapidly progressed to the stringent form embodied in these words. As I have suggested already, it is a form too stringent; but the truth lies nearer to it than to the milder phrasings earlier used, and therefore it is justifiable as a commencement.

Notice to begin with that, in the statement as just given, there is no allusion to the pressure or the volume. It is therefore asserted that, at the absolute zero, the entropy of a substance (of a single kind) does not depend on either. This I implied already in the caption to this section, by discarding the symbol $S(P, 0)$ which had previously served for the additive constant in (14), and replacing it by S_0 . From the general thermodynamic equations based on First and Second Laws, it can be shown that if this is true for any substance in particular, then certain measurable features of that substance—notably the coefficient of thermal expansion—must be zero at the absolute zero. Now it does appear to be a general rule that this coefficient, and the other features in question, are trending rapidly to zero at the lower end of the accessible range of temperatures; so this, the mildest form of the "Third Law," is well attested.

Notice then that in the statement as given there is no allusion to phase. Thus, if any substance can exist in both the solid and the liquid phase at the absolute zero, its entropy must be the same in both (if the theorem is true). If we insist on fluidity as a quality of a liquid, there is evidently just one such substance—helium, of course. It appears that for this case the theorem is true.⁴

⁴ At the lowest accessible temperatures, the divide between the "liquid" area and the "solid" area of the phase-diagram is running nearly parallel to the temperature axis, and heading for the ordinate 25 (in atmospheres) on the pressure-axis. Strict parallelism of the divide to the temperature-axis, which is probably realized just before the absolute zero, would imply equality of entropy in the two phases (by one of the thermodynamic equations hinted at above). Another item of evidence is cited on p. 72.

There are substances able to exist in two or more crystalline phases: tin and sulphur are probably the best-known examples. For some of these it is possible to start with one phase at a temperature extremely low: warm the substance up to a temperature of "transition," at which it changes reversibly into the other phase; and cool the new phase down to the temperature at which the experimenter started. Let me denote by S_1 the entropy at the commencement of this process; by S_2 the entropy at its finish; by C_{p1} and C_{p2} the specific heats of the two phases; by T_t the temperature of transition, by L_t the heat absorbed during the transition. We have:

$$S_2 - S_1 = \int_0^{T_t} (C_{p1}/T) dT + L_t/T_t - \int_0^{T_t} (C_{p2}/T) dT \quad (16)$$

According to Nernst's Theorem, S_2 and S_1 and consequently their difference should vanish if the extremely low temperature at start and finish were the absolute zero. We should therefore expect the right-hand member of this equation to be at any rate extremely small, if the temperature in question is at the bottom of the accessible range. Such is indeed the case.

It is very evident that the argument just given proves at the very most that the entropies of the two phases are equal at the absolute zero—not that either of them has the particular value *zero*. The like is true for the other arguments thus far cited; and indeed in the earliest phrasings of the "Third Law," no value was assigned to the entropy at the absolute zero—neither the value *zero*, nor any other. Why then are we to adopt, and presently seek to justify, the particular value *zero*? One part of the answer will be the climax of this paper. The other derives from the speculations as to the nature of entropy, which for half a century have been among the most deeply perplexed, the most difficult and the most fruitful of the divisions of theoretical physics.

There are two words which dominate these speculations: "probability" on the one hand, "disorder" on the other. Both of these are very familiar words with very familiar meanings, and some tinge of the familiar meaning is in each case carried over into the technical meaning. The technical meanings, are, however, abstruse; and cynical though it may sound, there is no exaggeration in saying that a large part of the speculation consists in trying to find meanings for the one and the other, which can be fruitfully used in the study of entropy. "Disorder" is the word which we shall examine first.

The familiar meaning of the word "disorder" leads straight to one useful consequence. Of all the possible or conceivable states of matter, the one which anybody would choose as the least disorderly is the crystalline state. But moreover, most people would deem the thermal agitation of the atoms in a crystal as a departure from order; therefore the colder the crystal, the

closer its approach to perfect order. Perfect order would consist in every atom located at rest in exactly its proper place in the crystalline lattice. If such is the state of affairs at the absolute zero, then a crystalline phase at the absolute zero exhibits perfect order. Now as I have implied without precisely saying, entropy is taken to be a measure of disorder. If this is proper, then it is sensible and correct to say that entropy vanishes for the perfect crystal at the absolute zero. This is a reason, it is in fact *the* reason, for assigning the value *zero* to the additive constant S_0 .

If I were to stop my exposition at this point, it would certainly be an impressive conclusion, but hardly a just one. We cannot solve the mysteries of entropy in any so simple a way; in fact they have never been completely solved. Many additions should be made to the foregoing paragraph: some would help out its evident meaning and some would not. Thus, as it stands, it certainly implies that a liquid at the absolute zero—helium offering such a case—must exhibit disorder and therefore have a greater value of entropy than does the crystalline solid. However, it turns out that liquid helium near the absolute zero has the same entropy as solid helium does, and therefore if one value is zero so also must the other be. If instead of liquid helium I had taken the supercooled and toughened liquid which is called a “glass”—glycerol or alcohol in the glassy state, for instance—the result would have been more agreeable. Several of these glasses have been studied with great care, and the right-hand member of equation (16) evaluated for them; it turns out that the entropy near the absolute zero is markedly and indubitably greater for the glass than for the crystal. “Disorder” must therefore prevail in the glass, but the result with liquid helium impedes the physicist from proclaiming that it is simply the obvious disorder of the irregular placing of the atoms in the glass. A mixture of two substances of a single kind, even when this mixture forms a beautiful crystal, may nevertheless present disorder; for the two kinds of atoms may be sprinkled in a thoroughly chaotic manner over the available points of the crystalline lattice. Such a mixture, it has been found, does have an entropy near the absolute zero which is definitely greater than the sum of the entropies of the two substances when unmixed. But it is also possible for the mixture of two substances to be orderly, in the usual sense of the word! Thus in a mixture—“alloy” is the customary word—of equal numbers of atoms of copper and zinc, the copper atoms may all be found upon one lattice and the zinc atoms upon another, the two lattices interpenetrating and interlocking with each other so as to form the lattice of the crystal of the alloy. This is one of the extreme possibilities: the other is, the entirely chaotic besprinkling of the points of the two lattices with atoms of the two kinds. Both can be realized, the transition between the two being

known as "the order-disorder transition." The entropy goes down as the transition is made from disorder into order.

The conclusion then is, that we may accept entropy as a measure of disorder and disorder as a way of visualizing entropy, provided that we are prepared to define "disorder" in ways which at least in certain striking cases do not depart impossibly far from its traditional meaning. A consequence of this attitude is, that it is plausible and sensible to attach the value *zero* to the constant here called S_0 , the entropy of any substance of a single kind in a crystalline phase at the absolute zero. The words "in a crystalline phase" are a reservation to the original statement. If further reservations become necessary, they will of course have to be made.

THE THEORY OF THE CONSTANT I .

To give even an inkling of the theory of the constant I , it is desirable to take "probability" as the word for which meanings must be found, not too distant from the popular meaning and yet fruitful for the study of entropy. Those who began this process were Gibbs and Boltzmann, working in the closing years of the nineteenth century. Their ideas have since undergone many a transformation, usually in the direction of greater adequacy but also (alas!) in that of greater difficulty. I will follow a route beginning as Boltzmann's did, but carried onward in a manner which became possible about thirty-five years ago, at the time when Nernst's Heat Theorem was being established. It does not lead us quite the whole way to the accepted value of I , so that at the end I shall have to make an extra step without doing more than to indicate whence its justification comes.

We begin by considering a gas in a container of volume V , in equilibrium with itself and with the outer world at a temperature T . "In equilibrium with itself" implies first of all that it is evenly spread throughout the volume of the container—surely one of the earliest of all inbred ideas concerning the behavior of gases. To give a quantitative meaning to this notion of the gas being evenly spread throughout the container, we imagine the volume divided into little compartments or cells of equal volume V_0 . The statement then is that the number of atoms in every cell is the same. Putting N for the total number of atoms and Nf_i for the number in the i th compartment,

$$f_i = \text{constant} = V_0/V \quad (17)$$

The quantity f_i is called the "probability" that an atom chosen at random shall be in the i th cell—the first occurrence of the word "probability" with a definite meaning in this discourse.

The next step is to define the entropy in the manner which follows:

$$S = -kN \sum f_i \ln f_i \quad (18)$$

a definition which in the case of the even distribution of the gas throughout the container reduces to this,

$$S = kN \ln V - kN \ln V_0 \quad (19)$$

This is of course a *tentative* definition, to be eschewed if ever it should lead us into contradiction with the known properties of entropy. As yet it leads us into none, for the term in $\ln V$ corresponds to a similar term in the description of entropy which equation (13) has already supplied. To make the two agree exactly, we have simply to assign a special value to the factor k ; and as will be seen at once, this value is

$$k = R/N_0 \quad (20)$$

N_0 standing for the number of atoms per mole, the Avogadro number. Though k is known as Boltzmann's constant, this evaluation was beyond Boltzmann's powers, for in his time the value of N_0 was not known.

The expression (19) contains no allusion to temperature. It is in fact not the entropy in full which has so far been defined, but only what I may call the "contribution of volume to entropy." We have now to account for the contribution of the kinetic energy of the molecules to the entropy of the gas. Thus far I have been able to come by adducing the deeply-ingrained conviction that a gas in equilibrium in a container is evenly spread throughout the container. There is no such widely-held conviction about the distribution-in-energy of the molecules of the gas; but to everyone who has studied physics for more than a year or two there will be nothing surprising in the formula which follows. It must be introduced by asking the reader to imagine a three-dimensional space, in which the variables along the three axes are identified not as coordinates in ordinary space, but as components of momentum p_x, p_y, p_z . The momentum which is meant is the momentum of the individual atom, and the axes x, y, z along which its components are taken are axes of a coordinate frame in ordinary space—they might be along three edges of the container, for instance. A point in the "momentum-space" represents an individual atom in respect of its momentum and therefore in respect of its energy, but not in respect of its position.

The momentum-space is now to be divided into compartments of equal volume H_0 ; but we are not to besprinkle its compartments uniformly with the dots representing the atoms! Instead, when comparing any two of the cells, say the i th and the j th, we are to write

$$f_i/f_j = \exp [-(E_i - E_j)/kT] \quad (21)$$

which reduces to the statement,

$$f_i = Z^{-1} \exp(-E_i/kT) \quad (22)$$

Z being a symbol for the sum,

$$Z = \sum_i \exp(-E_i/kT) \quad (23)$$

which, incidentally, is known as the "partition-function" or "state-sum" of the system—here, of the individual atom of the gas.

In these latest equations, E_i stands for the energy-value corresponding to some point in the i th cell. It is kinetic energy of translatory motion with which we are concerned; therefore E_i is given by the equation

$$E_i = (1/2m)[(p_x^2)_i + (p_y^2)_i + (p_z^2)_i] \quad (24)$$

where now the components of momentum are to be evaluated at some particular point in the i th cell. But at which particular point? And to go further back, just how are the cells of volume H_0 to be designed in the momentum-space? As cubical blocks with their edges parallel to the coordinate-axes, or how? There are problems in which definite answers must be given to these questions, but we shall be able to avoid them. It will be adequate here to conceive of the cells as cubical blocks and the value of E_i as the *average* value of the right-hand member of (24) in the i th cell.

Now we require from (24) the value of Z as defined in (23), to establish the values of f_i as given in (22), to yield finally the value of entropy as given in (18).

Let us form the integral

$$\iiint \exp(-E/kT) dp_x dp_y dp_z, \quad E = (1/2m)(p_x^2 + p_y^2 + p_z^2) \quad (25)$$

the range of integration extending over the whole of momentum-space. This integral may be described as follows. Let the momentum-space be divided into *cells of unit volume*. Each of these cells of unit volume makes a contribution

$$\exp(-\bar{E}/kT)$$

to the integral, \bar{E} standing now for the *average value of E in the cell in question*. The integral is the sum of all of these contributions. Now let us inquire how much of a contribution is made by this same cell of unit volume to the partition-function. This second contribution is made up of $1/H_0$ terms, one for each of the cells of volume H_0 which occupy the cell of unit volume. The values E_i corresponding to these cells will not be exactly equal to the value \bar{E} corresponding to the entire cell of unit volume;

but to the degree of approximation which is now being used, the difference may be neglected. The partition-function is then equal to $1/H_0$ times the integral (25). Now the value of the integral (25) is given in all tables of definite integrals, and in terms of our symbols it amounts to

$$(2\pi mkT)^{3/2}$$

We are now to divide this by H_0 , and proceed along the path which has been indicated.

The procedure is simple and straightforward. As a byproduct one finds the result that the energy of the gas—which I have earlier symbolized by U —is equal to $(3/2)kNT$. It follows that the specific heat at constant volume is equal to $(3/2)kN_0$ for one mole, to n times this value for n moles of gas. Utilizing this result, and putting nR for Nk wherever the latter occurs, one duly arrives at (18) all filled out in the proper way. This represents the contribution of the temperature to the entropy; now adding the contribution of the volume from (19), one arrives at *the entropy of n moles of the gas as function of temperature and of volume, as derived by the statistical method*:

$$S = nR \ln V + nC_v \ln T + nR \ln \frac{(2\pi m)^{3/2} k^{3/2}}{V_0 H_0} + (3/2)nR \quad (26)$$

This is now to be compared with the equation (13) for entropy as function of volume and of temperature, embodying the definition of entropy wherefrom we started.

So far as the dependence on T and on V is concerned, all is well! And there seems even to be a prospect of finding a formula for the additive constant. The prospect, though, is still befogged in two ways: by my lack of precision till now as to the magnitudes of V_0 and H_0 , and by the absence from (26) of any term convertible into the term $nR \ln(nR)$ which stands out so prominently in (13).

As to V_0 and H_0 : no assumption shall be made about either by itself, but it will be assumed that *their product is equal to Planck's constant h raised to the third power* (third power, because of the three dimensions of space):

$$V_0 H_0 = h^3 \quad (27)$$

This I will attempt to justify from a fact not even divined when the formula was made.

To divide the momentum-space into cells of definite size, and to allot to the partition-function just one term from each cell—this comes to the same thing as allowing certain discrete momentum-values to the atoms in question, and denying them all values intermediate to these "permitted"

ones. By using the words "permitted values" I am recalling the quantum-theory, and it is in fact a part of the quantum-theory which we are now employing, as betokened already by the entry of the symbol h . It is one of the oldest parts of the quantum-theory; but the new fact—comparatively new—is this. Atoms, like all other particles, are attended and governed by waves. These waves, when with their atoms they exist in a limited space such as that which the container offers to the gas, are constrained to what in acoustics is known as "resonance." Not every frequency of vibration is allowed to the air within an organ-pipe, to the wire of a piano or to the membrane of a drum, but only such as have wave-lengths fitting neatly into the compass of the cavity, the wire or the drumhead. The dimensions of these acoustical resonators control the permitted wave-lengths, and these in their turn determine the frequencies. In the case which we are now considering of a container filled with a gas, the dimensions of the container control the wave-lengths associated with the atoms, which are the wave-lengths of resonance. These in turn control the momenta of the atoms, because of the relation between the momentum of a particle and the wave-length of its associated waves—the "Rule of Correlation":

$$p = h/\lambda \quad (28)$$

To say that the momenta of the atoms are those and only those corresponding to the resonant wave-lengths, and to say that $V_0 H_0$ in (26) is equal to h^3 —these are equivalent statements. When the former is accepted, so perforce is the latter, and the additive constant in (26) is fully determined. But still it lacks the term $-nR \ln nR$ or $-Nk \ln Nk$ which figures in (13)!

To introduce this term into the theory in a way both logical and simple is not an easy task. The formula at which we are about to arrive is frequently known as the "Sackur-Tetrode formula" after the two physicists of whom (before the first world war) one was the first to approach and the other the first to reach it. Sackur assumed outright that $V_0 H_0$ is inversely proportional to N , while Tetrode subtracted from (26) a term $k \ln N!$ —the exclamation-point here not having its rhetorical meaning, but signifying that $N!$ is " N factorial," the product $1 \cdot 2 \cdot 3 \cdots N$. By Stirling's celebrated formula,

$$\ln N! = N \ln(N/e) \quad (29)$$

an approximation amply valid for such enormous values of N as are normally here considered. Be it noted that e here stands for the exponential base and not for the electron-charge (in the latter sense it is never used in this article).

To make clear the basis for this subtraction of $k \ln N!$ I should have to go far into the roots of the conception of entropy as probability. The best

I can do for the present is to follow Tetrode by saying that he deemed (26) as it stands to be an overstatement of the entropy, arising because in advancing from the underlying theory to equation (18) one assumes the atoms of the gas to be distinguishable, whereas actually for a substance of a single kind they are indistinguishable. In somewhat the same way one might overstate the entropy of a crystal by supposing it to be composed of atoms no two of which were alike, while actually it was a substance of a single kind. The subtraction of $k \ln N!$ was Tetrode's manner of correcting the overstatement. He did better than perhaps he knew, for while his reasons never commanded universal assent, his choice of a term to be subtracted was ratified first by experiment and then by the "new statistics" which made their appearance in physics some fifteen years ago.

Returning to (26): writing the last term of the right-hand member as $nR \ln e^{3/2}$, and consolidating it with the third term; introducing Tetrode's subtractive term; augmenting this last by a term $-nR \ln k$, and compensating by adding $+nR \ln k$ to the third term—doing all this, one finds,

$$S = nR \ln V + nC_v \ln T - nR \ln (nR) + nR \ln \frac{(2\pi m)^{3/2} k^{5/2} e^{5/2}}{h^3} \quad (30)$$

Now the additive constant is filled out completely, and ready for whatever test experiment may impose.

To prepare it for the test, we turn back first to equations (12) and (13), and note that the constant there denoted by nI is none other than the fourth term in the right-hand member of (30):

$$I = R \ln \frac{(2\pi m)^{3/2} k^{5/2} e^{5/2}}{h^3} \quad (31)$$

Continuing onward to (15) we are reminded that no theoretical statement about I is worth anything by itself, since all that data can supply is the value of the combination $(I - S_0)$. A hopeless situation, in appearance! But now it is high time to hearken to what the data say. The data say, to begin with:

For many monatomic gases, the right-hand member of equation (15) is equal to the "statistical" value of I .

This may be taken as meaning two things at once: that (a) the statistical theory of the entropy of a gas is right, and (b) the entropy of a solid (crystalline and of a single kind, for such are these solidified gases) is zero at the absolute zero. It is taken as meaning these things. It might of course also be taken as meaning that both statements are wrong by about the same amount, the errors compensating one another. But so unlikely does it seem that two such different theories should both be wrong and yet by precisely

the same amount, that I venture to say that few will be found who are critical enough to insist on the doubt.

This concordance might be shown by giving actual values of the right-hand member of (15), for actual gases at one or more points adjoining the curve which divides solid from gas on the phase-diagram. The usage is, however, different, and it is of some value to abide by the usage, even though I am now required to make one more transformation of (15) which I have hitherto avoided. This involves the auxiliary equation,

$$dL/dT = C_p^{gas} - C_p^{sol} \quad (32)$$

which makes it possible to calculate L for any temperature, provided it be measured at any other temperature and the specific heats be known at all the temperatures in between. We may thus start from any measured value of L , calculate a value L_0 appropriate to the absolute zero, and thereafter we may write the integrals, as always heretofore, extending from zero to T .

$$L = L_0 + \int C_p^{gas} dT - \int C_p^{sol} dT \quad (33)$$

The first of these two integrals is equal for a monatomic gas to $(5/2)RT$ per mole. Since it is L/T which appears in (15), this entails a term $(5/2)R$ on the right of that equation. This term neatly blots out the term $R \ln e^{5/2}$ which is a portion of our statistical value of I as given in (31), so that after all the equation is not much worsened in appearance. It has in fact assumed the form

$$R \ln P = -L_0/T + (5/2)R \ln T - \int (C_p^{sol}/T) dT + (1/T) \int C_p^{sol} dT + J \quad (34)$$

and here J is yet another additive constant—the additive constant of the vapor-pressure equation in its commonest form—of which this may be said,

$$J = R \ln \frac{(2\pi m)^{3/2} k^{5/2}}{h^3} \quad (35)$$

if the statistical theory is sound and if in addition the entropy of a crystalline solid of a single kind at the absolute zero is zero.

It is evident that if the two presumptions are true, then the remainder left behind when $(3/2) \ln m$ is subtracted from the experimental value of J will have a definite value, the same for all gases. This indicates how the test is made, or rather how it is set forth in the literature. The remainder, expressed in units which need not concern us, should be -1.589 . Now,

data are available⁵ for all of the noble gases from helium through xenon; and I quote the values which they furnish for this "remainder":

He 1.59 ± 0.01 ; Ne (two experiments) 1.56 ± 0.04 , 1.59 ± 0.01
 Ar (two experiments) 1.61 and 1.61 ± 0.04 ;
 Kr 1.59 ± 0.02 ; Xe 1.588

The agreements are remarkably good, and when one remembers the contrast and the subtlety of the two theories which they ratify conjointly, one deems them among the most impressive in the whole of physics or of chemistry either. The result for He implies that $S_0 = 0$ for *liquid* helium.

There are data available also for the vapors of several metals, though for these the experimentalist's task is much harder. It will be seen that in most of the cases we may again rejoice in agreements, though within a broader range of experimental unsureness; in a few there is disagreement, and one can only wonder whether the measurer of vapor-pressure underestimated his possible error.

Na (two experiments) 1.57 ± 0.1 and 1.41 ± 0.03 ;
 K 1.47 ± 0.04 ; Mg. 1.61 ± 0.2 ; Zn 1.51 ± 0.15 ;
 Cd (two experiments) 1.63 ± 0.1 , 1.51 ± 0.1 ; Hg 1.62 ± 0.03 ;
 Tl 1.40 ± 0.3 ; Pb (two experiments) 1.7 ± 0.2 , 1.21 ± 0.26 .

So the situation with respect to monatomic gases is satisfactory on the whole and almost unblemished.⁶ But monatomic gases are but a small proportion of all vapors: has not the theory something to say as regards those which are diatomic—such as oxygen, hydrogen, nitrogen, carbon monoxide—and even those which are polyatomic?

The theory does indeed cover these; and the needed enlargement is simple to write down, if not always easy to compute. Thus far the partition-function has contained only the terms supplied by the translatory motions of the molecules in the container—terms which depend on no other quality of the molecules than their masses, and for a given mass are the same whether the molecule is composed of a single atom or of two or of many. Now to the partition-function so composed are to be added the terms deriving from the rotation and from the vibrations of the molecules. Each new term is of the familiar form $\exp(-E_i/kT)$, where now E_i is to stand for some permitted energy-value of rotation or of vibration, and the summation is

⁵ Data from the collation of Ditchburn and Gilmour (*Rev. Mod. Phys.* 13, 310, 1941), except the value for xenon which is from Clusius.

⁶ Here I must say, even if only in a footnote, that for atoms which have angular momentum there is still one more term in the additive constant occurring in the right-hand member of (30). This term may be loosely described as referring to the "disorder" arising from the fact that there are two or more different orientations of the angular momentum, between which the atoms may choose. Its exact value (zero for the inert gases, $nR \ln 2$ for the alkali metals) is derived from the spectrum of the atom. Allowance is made for this term in the computation leading to the value of the "remainder", and the agreements here tabulated for Na and K sustain the allowance. A bad disagreement for tungsten emerges from an early (1924) research by Lange.

to be carried over all values of E_i . There is less of a mental obstacle now than there was in the "translatory" terms, for the doctrine of discrete permitted energy-values in rotation is among the oldest, while that of discrete energy-states in vibration is quite the oldest, of the whole of quantum-theory. To get the energy-values E_i , the spectra are consulted. Spectrum analysis is the most highly-developed of the branches of physics, and the knowledge of the values of E_i which it affords for the better-known of the diatomic molecules—and even for some few of the triatomic—may be described as complete, daring as it may sound.

Values of entropy figured by the statistical way which I have been describing, with additions duly made to the partition-function to allow for rotation and vibration, are called "spectroscopic" entropy-values by Giauque and his colleagues of the Berkeley school. As a rule they are computed for a standard pressure and temperature, often for one atmosphere and 25°C.; let us call these P_0 and T_0 . Now as a rule the point (P_0, T_0) does not lie just off the divide which on the phase-diagram separates solid (or liquid) from gas. One may, however, use (11) for getting the entropy-difference between (P_0, T_0) and any such point (P, T) lying along the divide on the side corresponding to gas. At the point (P, T) the entropy may be evaluated by the right-hand member of (14), and to it may then be added the entropy-difference just mentioned. The sum, *computed with the assumption that S_0 is zero*, is what Giauque and his school name a "calorimetric" entropy-value. If the two agree, there is a verification of the conjoined assumptions that the statistical theory is sound, and that the crystalline solid at zero absolute has none of that disorder which is the source of entropy.

I take the following data from Eastman⁷ of the Berkeley school. Of his two tables, one comprising gases for which the data are definitely better known than they are for the rest, I quote this one only. The accuracy of the calorimetric value "is in all cases high, errors being of the order of 0.1 throughout." The supposed accuracy of the spectroscopic values is indicated by the number of significant figures to which they are carried.

	<i>Calor.</i>	<i>Spectrosc.</i>
N ₂	45.9	45.788
O ₂	49.1	49.03
HCl	44.5	44.64
HBr	47.6	47.48
HI	49.5	49.4
CO	46.2	47.316
NO	43.0	43.75
H ₂ O	44.23	45.17
N ₂ O	51.44	52.581
H ₂	29.7	31.23

⁷ *Chem. Rev.* 18, 257 (1936).

The first five are the stellar examples of concordance, therefore support for the two conjoined assumptions. In the last five the discrepancy is deemed to exceed the possibility of doubt, and some explanation ought to be found.

How is one to explain a "calorimetric" value less than the "spectroscopic"—as occurs in all five of these cases? The comparison, I recall, is essentially between $(I - S_0)$ and I . In all of these five cases, $I - S_0$ turns out to be less than I ; therefore we are tempted to assume a "disorder" in the solid, subsisting even unto the absolute zero. The case of hydrogen is the clearest, the disorder being traceable in part to the intermingling of two types of hydrogen molecule known as the "ortho" and the "para" type. In the other cases, the explanations have a vagueness which suggests that they are speculative. This is not a very satisfactory statement to end with. Yet even these discrepancies are so small, that even if there were no closer agreements one would still feel assured that the truth is to be found in some minor alteration of the theory rather in rejecting the theory altogether; and the five excellent agreements, combined with the excellent agreements for so many monatomic gases, convert this feeling of assurance into certitude.