THE THIRD LAW OF THERMODYNAMICS

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The developments of modern theory and experiment in the field of the third law of thermodynamics have been of a character originally difficult to foresee. During the course of them many shifts in emphasis of particular phases of the subject have, of course, occurred. It remains true, however, that the ideas brought forth in the first few years following its announcement have given rise to more or less continuous discussion, extending into the last decade, and can scarcely be neglected in any summary of the present situation. They may be outlined in historical sequence somewhat as follows:

EARLY DEVELOPMENTS

1. In 1906 Nernst published his famous "heat theorem" as the consummation of the long-cherished ambition of the chemist to determine affinities from purely thermal data. The essence of the theorem and the most general of the early statements of it is that the entropy change accompanying a change in state approaches zero as the absolute zero of temperature is approached. More briefly (and less precisely)

$$\Delta S_0 = 0 \tag{1}$$

2. Originally the theorem was restricted to condensed systems. For the treatment of systems involving gases Nernst in 1908 invented his "chemical constants."

3. Nernst next, in 1910, in searching for a form of statement resembling the empirical ones for the first and second laws, adopted the "principle of the unattainability of the absolute zero."

4. About this time, Planck proposed and began the statistical interpretation of the concept of absolute entropy, leading to the formulation of the third law in terms of the entropy of individual phases as

$$S_0 = 0 \tag{2}$$

5. In 1912 we find the question of the entropy of supercooled liquids and solid solutions being debated. Nernst believed that phases of these types

might be included with the crystalline, and assigned zero entropy, while Planck and Einstein held that solid solutions at least should be assigned positive entropy.

6. In 1913 Polányi recognized that the effect upon entropy of increasing pressure should be much the same as that of decreasing temperature and that entropy changes at finite temperatures probably approach zero at infinite pressure.

7. Finally, beginning about 1913, the questions of "gas degeneracy" and the statistical calculation of the entropy constants were developed by various authors, bringing gases within the scope of the law in a broad sense.

RECENT DISAGREEMENTS OF OPINION

As so often happens, the underlying stimulus throughout these developments was provided not only by their importance but in no small part also by their controversial nature. It is, however, surprising to find to what extent this controversial element in the form of varying opinion as to validity and utility of the ideas, and differences in interpretation and usage, has persisted to the present time.

In illustration, divergent views from two recent treatments of the subject will be quoted. In 1930, Simon (44) concludes his very able monograph with these words: "*the Nernst Heat Theorem is a generally valid principle, which may properly be called the Third Law of Thermodynamics.*" In 1932, Fowler and Sterne (10), in their discussion of statistical mechanics applied to the calculation of entropies, make the following summarizing statement: "We reach therefore the rather ruthless conclusion that *Nernst's Heat Theorem strictly applied may or may not be true, but is always irrelevant and useless—applied to 'ideal solid states' at the absolute zero which are physically useful concepts the theorem though often true is sometimes false, and failing in generality must be rejected altogether.*"

Examination of the contexts of the above extracts lessens the sharpness of their divergence. Even allowing for this, a real difference remains, and the same is true among other authors in several important questions of interpretation, although in any practical sense there is general agreement and understanding.

OBJECTIVES IN THIS REVIEW

It is the purpose of the ensuing discussion to show the present status of the third law in its various ramifications, particularly as affected by the work of the last ten or twelve years. The experimental situation will be summarized, and each of the seven topics of the first section will be touched upon, in greater or less detail, in an order dictated mainly by convenience. Thus, since the chemical constants and the absolute entropies are much used in recording results, these will be briefly touched on in the beginning. Some ideas important to the understanding of certain experimental effects will next be taken up. The experimental material, followed by a discussion of its interpretation, will then be presented, together with some further points respecting usage.

CONCERNING CHEMICAL CONSTANTS

The short-comings of the chemical constants have been pointed out by Lewis and Randall (34). Most serious of these, perhaps, is the fact that they treat of an unnecessarily restricted phase of the question. In addition they introduce distasteful procedures of an empirical character which have often been badly handled, and they permit a certain adjustment between auxiliary constants which may obscure the degree of agreement in comparisons of them. These disadvantages are not sufficiently offset by slight gains in convenience in certain limited connections. In spite of this their use continues in the traditional manner by many authors. A very desirable simplification and unification would be introduced if their use were discontinued in favor of the better methods of treating the important thermodynamic properties of gases that have long been known and used. Definite progress in this direction, but not as much as might have been hoped for, can be reported. Numerical values of these constants will not be cited in this work.

ABSOLUTE AND RELATIVE ENTROPY IN THERMODYNAMICS AND QUANTUM STATISTICS

The proposal by Planck of the idea of absolute entropy initiated a long-continued discussion of its validity and usefulness.

Thermodynamically, of course, entropy is defined only to a constant, and entropy changes are therefore the only quantities necessary or significant for purely thermodynamic purposes. The third law in the form of equation 1 strictly requires only that the entropy of the phases to which it applies approach a common value at absolute zero. Planck's contribution, as far as thermodynamics alone is concerned, consists in the recognition that zero is the most natural choice of this common limit, though only questions of convenience can be involved.

Statistically, Planck (38) ultimately reached the conclusion that the entropy is given by

$$S = k \ln W \tag{3}$$

where W represents the number of detailed states or configurations in which a system of fixed energy may exist. With the contributions of modern theory as to what constitutes distinguishable states, it has been shown by various authors (33, 42) and is generally agreed that this equation does in fact bring the thermodynamic and statistical concepts of entropy into correct relationship. The question of the undetermined additive constant is again unsettled in a rigorous sense (9), but the assumption of any value for it other than zero is forced indeed. One may therefore always, though he need never, assume it to be zero. In the absence of significance of any other assumption, and in view of the simplicity and value of the physical picture and the unquestioned practical convenience so obtained, it appears an excess of conservatism not to make this extension of the entropy concept.

In using absolute entropies it is always recognized of course that the assumed zero of the scale may be subject to modification with advancing knowledge. It may often also prove convenient to adopt a reference scale which will not include certain factors which remain unchanged before and after all reactions of common interest. This is in fact being done at the present time when "practical" entropies are tabulated which do not include certain known effects.

QUANTUM STATISTICAL INTERPRETATION OF THE THIRD LAW

A system consisting of N similar particles cooled to the neighborhood of the absolute zero under conditions which permit the attainment of stable equilibrium at all stages will ultimately reach a condition in which all particles, and the system as a whole, are in the lowest energy level. If in this condition a single state or configuration of the system is represented, the entropy will be zero in accordance with equation 3.

If, however, two or more physically different states of identical energy of the particles are possible, W of equation 3 will no longer be equal to unity, nor the entropy to zero. If the number of states of equal energy accessible to the particles, or their "degeneracy,"[1] is represented by g, the number of distributions of the particles between these states will be g^N, and the entropy by equation 3 is $Nk \ln g$, or per mole

$$S = R \ln g \tag{4}$$

The question of the validity of the third law resolves itself therefore in such cases into the question of the singleness or degeneracy of the lowest energy state of the particles.

Again, if the system be composed of N particles of two or more kinds, of mole fractions X_1, X_2, etc., physically different states in number equal to $N!/(X_1N)!(X_2N)! \ldots$ may be formed by permutation of the unlike particles.

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[1] It is unfortunate that degeneracy as here used is diametrically opposed in significance to the phenomenon of gas degeneracy, which implies a loss of multiplicity. In spite of the opportunity for confusion the traditional usage will be followed.

If near the absolute zero these configurations all have identical energy, W in equation 3 for the system in the state of lowest energy is given by this expression. With the aid of Stirling's theorem we then find

$$S = -R\Sigma X \ln X \qquad (5)$$

This is the much discussed "entropy of mixing" which should be shown by solid solutions at the absolute zero.

With these preliminary statements for reference during the comparisons, the experimental results thus far available will next be presented in summarized form, after which the above points will be returned to and in part amplified.

EXPERIMENTAL STATUS OF THE THIRD LAW

In presenting the experimental material we shall make use of the previous summaries of Simon (44), adding to them any significant data of more recent date. (Sources will in general not be cited unless they cannot be traced through reference 44.)

1. Direct determinations of entropy changes at low temperatures

There is a considerable group of phenomena by which the demands of equation 1 may be directly checked by observations of various temperature coefficients at low temperatures. These coefficients are all related to the entropy changes in the corresponding changes in state and should approach zero at absolute zero if the third law in the form of equation 1 is valid. In all cases they appear to do so, and afford important confirmation of the law in very diverse applications.

Thus the coefficient of thermal expansion has been studied for a number of substances down to temperatures sufficiently low to indicate its zero value at absolute zero. Substances studied include, for example, aluminum (5), diamond, sodium chloride (5), silicon dioxide (5), calcium fluoride, FeS_2, and Pyrex glass (5) to liquid air temperatures, and silver, copper, and Jena glass to liquid hydrogen temperatures.

The temperature coefficient of magnetic susceptibility for paramagnetic and diamagnetic substances and the spontaneous magnetization of ferromagnetic substances also obey the demands of the law. The paramagnetic substances are particularly interesting in this connection, since the temperature at which the coefficients become zero varies widely. It is already reached at room temperature in some of the metals. It persists in certain salts to very low temperatures, becoming zero at liquid helium temperature for some of these but following approximately Curie's law at these temperatures for others. The latter are the substances now being employed for the production of very low temperatures. At sufficiently low temperatures even these will undoubtedly approach zero values.

Two other effects differing widely from the above and from each other, namely the temperature coefficient of electrical polarization in dielectrics and the thermoelectric power of metals, approach zero values with the temperature. They also therefore afford interesting confirmation of the law.

The one substance, helium, that remains liquid to the lowest temperatures studied, permits several interesting tests. Thus the surface tension and density of the liquid, and the equilibrium pressure for the crystal–liquid transition all approach temperature invariance as demanded by the theorem.

2. Gas degeneracy

We shall depart temporarily from the consideration of experimental data to mention the case of gas degeneracy, since it is analogous to the foregoing examples in that it requires a zero value of the pressure–temperature coefficient of gases at constant volume as the temperature approaches zero. The theory is now established and shows that for a gas obeying Bose-Einstein statistics the pressure should approach zero tangentially and for one following Fermi-Dirac statistics the pressure should approach a finite value but again with zero slope. Simon (44) gives an interesting discussion of the possibilities for experimental verification of such a tendency, and its recognition in other related phenomena. These lie on the border of the practicable at the present, but appear to offer definite hope of results in the future. The results in qualitative accord with theory obtained by treating electrons in metals as degenerate (whether one chooses to call them "gaseous" or not) should also be mentioned.

3. Entropies of transition of crystals

Of the reactions which cannot be directly studied at low temperatures, the crystallographic transitions, because of the small number of necessary experimental measurements involved, were among the first to receive attention. The earlier determinations include the rhombic–monoclinic sulfur, white tin–gray tin, quartz–cristobalite, and calcite–aragonite transitions. The accuracy of the measurements is not high in most of these cases. It is best for the tin transition, which offers satisfactory agreement with the theorem. This appears to be true of the other cases also to the extent that differences from zero of the entropy change at absolute zero as large as $R \ln 2$ (compare equation 4) are precluded.

To this older list may be added the two forms of cyclohexanol (28). Also, new determinations of heat capacities of rhombic and monoclinic sulfur (as yet unpublished) have recently been completed in this laboratory by McGavock, bringing this classic case into the group of accurate checks of the law.

4. Crystal–liquid transitions

Liquid helium at the absolute zero, as mentioned above, appears to have zero entropy. All others that have been studied exist at low temperatures in the supercooled condition. These "glasses" without exception show positive entropies in varying amount at absolute zero. The most thoroughly investigated case is that of glycerol glass, for which the molal entropy at 0°K. appears to be 4.6 E.U. The corresponding entropy of ethyl alcohol glass is about 2.6 E.U. For quartz glass the value is about 1 E.U. Other less completely investigated substances show similar effects.

5. Entropy of solutions

A complete investigation of a glassy solution of glycerol and water, in which specific heats were measured down to 9°K., was made by Simon. The reaction studied may be written, per "mole" of the final solution,

$$0.470C_3H_5(OH)_3 \cdot 0.032H_2O(\text{liq. sol.}) + 0.498H_2O(\text{ice}) = 0.470C_3H_5(OH)_3 \cdot 0.530H_2O(\text{liq. sol.})$$

The measured value of ΔS for this reaction at 273°K. was 3.55 cal. per degree. In conjunction with the specific heat data, this gave as the difference in entropy of the two solutions at 0°K. 1.30 ± 0.36 cal. per degree. The value of this difference calculated by equation 5 is 1.14 cal. per degree.

Earlier investigations by Gibson, Parks, and Latimer on mixtures of ethyl and propyl alcohols showed that to liquid air temperatures at least the heat capacity of the glassy solution is approximately an additive function of those of the pure glasses, indicating a positive entropy for the solution at absolute zero.

Of crystalline solutions only one system has been experimentally investigated. Eastman and Milner (7) found for the reaction

$$0.728AgBr(\text{cryst.}) + 0.272AgCl(\text{cryst.}) = 0.728AgBr \cdot 0.272AgCl(\text{cryst. solution})$$

that ΔS at 298°K. is 1.12 ± 0.1 cal. per degree, as compared with the calculated value (equation 5) 1.16. From the specific heat data the value found for the absolute zero was 1.03, within the error therefore unchanged from the above. In view of the simple specific heat laws obtaining for crystals, extrapolation to the absolute zero involves less uncertainty than usual. This example offers, therefore, particularly strong confirmation of the belief that the entropy of mixing is present in all such phases at the absolute zero.

6. Entropy changes in chemical reactions

Numerous reactions of varied types, including heterogeneous reactions involving crystals only, and heterogeneous and homogeneous gas reactions, have been studied from the standpoint of the third law. High accuracy is in general difficult of attainment, because independent determinations of changes in heat content and free energy and the individual heat capacities of all reactants and products are often necessary, and because the exact identity of the solid phases in the various measurements cannot always be assured. When the entropy change can be directly determined from temperature coefficients of electromotive force, as is often possible, the uncertainties are greatly reduced.

Concerning the reactions in condensed systems, it may be said that in all cases the third law is verified within the error of measurement. In a majority of them the error is sufficiently small to make entropy changes at absolute zero of the order of R ln 2 extremely improbable, and in perhaps a half dozen of the reactions the law is substantiated within 0.2 or 0.3 E.U.

In the gas reactions, which comprise a larger and more important group, a similar statement may be made, with a few exceptions where apparent disagreement occurs. As the comparison of individual entropies of the gases, to be discussed below, is a more decisive test of the law, and since the reactions for which disagreements are most apparent involve substances which also show the effect individually, no list of the numerous reactions studied will be given here, and the discussion of the apparent anomalies will be deferred. Compilations of data may be found in the summaries by Simon (44).

It should be mentioned also that many reactions used by Latimer and his associates in estimation of entropies of ions constitute checks, often of high accuracy, of the third law. These reactions have been conveniently tabulated by Latimer, Schutz, and Hicks (30).

7. Comparison of entropies of gases calculated quantum-statistically with values derived by application of the third law

The important contributions of wave mechanics to the older quantum-statistical theory are: the unambiguousd efinition of W in equation 3 as the number of (linearly independent) wave functions necessary for the representation of the possible states of a system; the correct assignment of the multiplicity of degenerate rotational states, and electronic and nuclear spin multiplicities; the justification and explanation of "symmetry numbers" in treatment of rotational states; the recognition of the non-combining ortho and para forms of molecules containing two (or more) similar atoms having a nuclear spin; and the proof that nuclear spin entropies cancel in reactions at ordinary and high temperatures, making possible the assignment of "practical entropies" neglecting them.

The classical calculations of the entropy constants of monatomic gases fortuitously were first applied to substances of no electronic degeneracy.

The agreement obtained with the experimental (third law) values was therefore satisfactory. For such vapors as the alkali metals and the monatomic halogens and others the multiplicity of the lowest electronic level contributes to the entropy. When this is taken into account, as determined spectroscopically, agreement is found throughout between the calculated and third law values within the error of measurement, which is in general small. The list of elements studied to date includes: helium (25), neon, argon, krypton (27), sodium, potassium, copper, silver, gold, zinc, cadmium, mercury, carbon, lead, tungsten, chlorine, bromine, iodine. The data in the literature are often compared in the form of the chemical constants, and will not be given in detail here.

In diatomic and polyatomic gases any of the factors mentioned in the opening paragraph of this section may be of importance in particular instances. A summary of entropies obtained by the application of the third law and by statistical calculation on the basis of spectroscopic evidence is presented in tables 1 and 2. The spectroscopic entropies do not include nuclear spin terms and are therefore the practical values. The temperature of comparison is 298.1°K., except for nitric oxide, where it is 121.36°K. The accuracy of the calorimetric measurements in table 1 is in all cases high, errors being of the order of 0.1 E.U. throughout.

TABLE 1

Molal entropy of gases

SUBSTANCE	ENTROPY (CALORIMETRIC)	ENTROPY (SPECTROSCOPIC)	REFERENCES
H_2	29.7	31.23	(11, 16)
N_2	45.9	45.788	(15)
O_2	49.1	49.03	(17)
HCl	44.5	44.64	(19)
HBr	47.6	47.48	(20)
HI	49.5	49.4	(21)
CO	46.2	47.316	(6)
NO	43.0	43.75	(23)
H_2O	44.23	45.17	(13)
N_2O	51.44	52.581	(3)

For a number of gaseous substances not included in table 1 calorimetric entropies of less accuracy or completeness in certain phases may be compared with statistical values. These are listed in table 2. For bromine and iodine the calorimetric entropy of the liquid and solid, taken from the compilation of Kelley (29), has been supplemented for the purpose of this comparison by vaporization entropies obtained from Lewis and Randall (34). It should be said that Giauque (12) has shown that the spectroscopic calculation confirms the calorimetric entropy of solid iodine within 0.1 E.U. Much of the discrepancy shown in the table is in this case therefore connected with the entropy of vaporization. This is probably also true of the other halogens. Pending the appearance of more accurate investigations of several of the substances in the table, little weight can be given the calorimetric entropies for third law comparisons.

In the figures for hydrogen, deuterium, carbon monoxide, nitric oxide, nitrous oxide, and water, tables 1 and 2 contain the only examples now known of crystalline systems of "one component" which appear to deviate from the third law by amounts definitely larger than the experimental error. These discrepancies are however explainable along lines discussed later.

The close agreement, taking into account the explanation of the "exceptions," of the calorimetric and spectroscopic entropies shown in table 1 constitutes perhaps the most accurate and convincing proof of the validity of the third law provided by any one method of testing it. At the same time the possibility of applying spectroscopic data to the calculation of entropy, which affords this excellent substantiation of the law, constitutes a direct threat to its future usefulness. Thus, there is little point in the purely calorimetric determination of affinity if it can be done with greater accuracy and convenience by other methods. The spectroscopic method is unquestionably capable of great extension and is destined to take a predominant part in future determinations of entropies. On the other hand, there will always be many substances which will not be susceptible of this treatment, and for them the calorimetric method will retain its importance.

TABLE 2

Molal entropy of gases

SUBSTANCE	ENTROPY (CALORIMETRIC)	ENTROPY (SPECTROSCOPIC)	REFERENCES
D_2	33.65	34.36	(8, 24)
Cl_2	52.8 ± 0.4	53.310	(18, 29)
Br_2	59.5	58.667	(19, 22)
I_2	63.1	62.29	(12, 19)
CO_2	52.4	51.07	(1, 19, 26)
NH_3	47.2 ± 1.0	46.4	(14, 19)
CH_4	44.3	44.35	(14)

Moreover, even in those cases where more accurate and convenient methods can be applied, the comparison with third law entropies permits interesting conclusions concerning phenomena occurring in the crystals. The "exceptions" cited above are examples of this, since for some of them the comparisons suggested conditions within the crystals (see below) which might otherwise not have been brought to light. In other cases, for example, hydrogen (and the hydrogen halides and others), the question of the presence or absence of molecular rotation within the crystal has been answered by comparisons of this kind. Also the general agreement of the third law and the statistical values of the entropy when nuclear spin effects are neglected shows that the spin orientations in crystals are still indefinite at the lowest temperatures of measurement. As a further illustration of the value of low temperature heat capacity studies, the suggestion by Simon (44) of the possibility of deciding by means of them whether the rotational levels in crystalline hydrogen remain completely degenerate at very low temperatures, may be mentioned.

INTERPRETATION OF EXPERIMENTAL DATA

The data summarized in the last section may be interpreted in connection with equations 1 to 5 as follows.

In the great majority of the many cases involving pure crystalline substances equations 1 and 2 are found definitely to hold and the entropies at the absolute zero may be taken as zero. In conjunction with equations 3 and 4, and neglecting nuclear spin degeneracy, this means that in these crystals the states obtained by ordinary methods of cooling to very low temperatures are statistically single. (The possibility that multiplicity exists but is the same in all cases may be dismissed as unlikely.) In considering the experimental confirmation of the third law from this angle, Schottky (41) has suggested that even though a molecule possess an intrinsic degeneracy this is resolved by the crystalline forces. There is some evidence (44) for this in the work of Simon, Mendelssohn, and Ruheman (47) concerning the heat capacities of mixtures of ortho- and para-hydrogen at very low temperatures. A theoretical treatment of the degeneracy of vibrational levels in crystal lattices has been attempted by Ludloff (35), who applied quantum statistical methods to a simple model. His result was that multiplicity of a high order appears in certain "lattice terms," but that the lowest level (in his model) is single.

The experimental evidence that solid solutions must be assigned finite positive entropy at absolute zero is also definite. The amount of this entropy proves to be calculable by equation 5. The agreement with the formula is not detectably affected by the fact that in the real, as contrasted with the ideal, solid solutions all of the various exemplars do not have identical energies. We are, in the real cases, not dealing with as sharp or complete a degeneracy of the system. The manner of formation of these "frozen" phases, nevertheless, requires the inclusion of the same number of configurations in the definition of the macro-state as for the ideal unconstrained system. The statistical multiplicity is therefore the same in the two cases, and equation 5 equally applicable to the entropy. The quantum-mechanical aspects of this question will be mentioned later.

The interpretation of the entropy of glasses, at absolute zero, which has been seen also to be well established experimentally, is not so straightforward as for the solid solutions. It is no doubt to be associated with the existence of several quantum states of nearly equal energy of the molecules in the glass, due to slight differences in orientation or relative position. The molecules are therefore probably to be treated as possessing a degeneracy (again not sharp) and handled by means of equation 4. (See also in this connection the work of Pauling and Tolman (37).) The advance prediction of the value of g in this equation (better, perhaps, the average value computed from the total number of states possible for the system as a whole) is not, however, possible. Working backward from the observed entropies its "apparent" value (only integral values are strictly significant) is found to be about 10 for glycerol, 3.7 for ethyl alcohol, and 1.6 for quartz glass. We are again dealing in these examples with frozen phases, in which the constraints require the recognition of a large number of possible exemplars at absolute zero, and a statistical multiplicity.

The indefiniteness of state in glasses and solid solutions, and the corresponding entropy, is often associated with a randomness (34) or lack of order (44, 45) in distribution of molecules. Insofar as these terms are taken to imply a multiplicity of possible quantum states of nearly equal energies, as outlined above, there can be no objection to this usage. The words are, however, susceptible of interpretation as a geometrical complexity or irregularity of arrangement of molecules in a single state. Such complexity will in general be accompanied by increased possibilities for additional states, justifying the association of terms. In itself, however, this factor seems to have no necessary or demonstrable connection with entropy (cf. ref. 7, p. 454). The interesting example of liquid helium near the absolute zero mentioned above may constitute a case in point. Evidence is accumulating (46) which eventually may determine the nature of this state. It is conceivable that it will prove not to possess any perfect order. It is already demonstrated to have zero entropy. The important thing is, therefore, that a single quantum state is represented, regardless of the interest that may attach to the visualization of this state. Compare in this connection the suggestion of Rodebush (40).

Turning to the "exceptions" of tables 1 and 2, Giauque and his associates have proposed (3, 6, 23) explanations for three of them. In carbon monoxide, nitric oxide, and nitrous oxide, they assume the existence of nearly equivalent states producible by end-for-end rotational displacement of the molecules, and that under the condition of formation the crystal does not distinguish between these states. By assuming the predictable values of g in equation 4 one obtains entropies of the right magnitude. The explanation is therefore plausible.

For water, Pauling, in a note soon to appear, has proposed an indefiniteness in the position of certain hydrogen bonds in the crystal as a more probable explanation than the earlier suggestion of Giauque and Ashley (13) of rotating molecules in the crystal. The value of g in equation 4 predicted by either of these pictures is approximately correct in magnitude. Experimental decision between them seems possible and may be awaited with interest.

The resolution of the long standing discrepancy of hydrogen exhibited in table 1 became possible only with the advent of wave mechanics. "Normal" hydrogen crystals are now known to be a solid solution in the proportion of 1 to 3 molecules of the "para" and "ortho" forms resulting from opposed and parallel nuclear spins. The para molecules are not rotating and have no degeneracy. The ortho molecules do rotate in the crystal and have a combined rotational and spin degeneracy of 9. The entropy of such crystals is obtained therefore by combining the "degeneracy entropy," $S = \frac{3}{4} R \ln 9$ (equation 4) with the "permutation entropy," $S = -\frac{1}{4} R \ln \frac{1}{4} - \frac{3}{4} R \ln \frac{3}{4}$ (equation 5). The value 4.39 E.U. so obtained, added to the third law value, gives the correct absolute entropy of the gas, 33.98 E.U. To obtain the "practical entropy" given in table 1 the high temperature spin entropy, $R \ln 4$, is deducted. For full discussion of these points the work of Giauque (11, 16) and Fowler and Sterne (10) may be consulted. It is interesting that at helium temperatures, the hydrogen begins to dispose of some of the entropy corresponding to the above terms (44). The calorimetric entropy in table 1 is based on extrapolations from temperatures where this effect is not yet manifest.

Deuterium is the only isotope hitherto separated from the naturally occurring mixture and experimentally studied by third law methods. In a general way the state in normal deuterium crystals at low temperatures is analogous to that of normal hydrogen, though the proportions and multiplicities of the ortho and para forms are interestingly different. Taking these into account the experimental and statistical determinations of entropy are again in good agreement (8).

The natural occurrence of isotopic mixtures in many elements and their compounds introduces, in a strict sense, a multiplicity and entropy in their frozen crystals at low temperatures. These differ in no essential way from any other solutions, so far as third law considerations are concerned. Since the proportions of the mixtures do not change significantly in chemical reactions this effect need not be included in the practical entropies. In artificially prepared mixtures of comparable proportions of hydrogen and deuterium and their compounds, appreciable differences in mole fraction of the various molecular types may result in reactions. This may introduce slight effects in the mixing terms in third law calculations relating to such mixtures, which are however not of practical importance. It should be said that the purely statistical treatment of entropy effects in isotopic mixtures involves many interesting points concerning spin and rotational multiplicities and the occurrence or non-occurrence of ortho and para forms in the different molecular types. The examples of chlorine (18) and hydrogen–deuterium mixtures (24) may be cited. These effects are not directly connected with the third law and will not be discussed here.

The interpretation of the entropy of the "frozen" phases discussed above introduces, of course, a limitation of the third law as expressed by equations 1 and 2. It nevertheless appears to meet successfully and satisfactorily all thermodynamic and statistical requirements. Many authors (44), however, prefer to preserve the generality of these equations by excluding frozen phases from thermodynamic consideration. Their basis for this is that the constraints in these systems cannot be rigidly maintained. Ideally reversible isothermal processes involving them cannot therefore be carried out, and no significant entropy changes determined by such processes, because of shifts with time toward the stable states (44, 45).

It is true that complete thermodynamic equilibrium is not established in these phases. For their definition, not only the numbers and kinds of atoms and the energy and volume of the system, which ordinarily suffice, but some additional specification, such as the temperature or a statement of constraints, must also be included. Once this is done, and adhered to, thermodynamics may be successfully applied, and often is in many actual systems. The element of time, except as the uncertainty principle may be involved, then does not enter in any significant sense (32). It appears an unnecessary limitation to exclude such treatment completely from thermodynamics. These questions have been discussed at some length by Eastman and Milner (7), and need not now be further elaborated.

It remains, however, to mention the behavior predicted by wave mechanics for ideal solutions and constrained systems such as real solutions and glasses on cooling to temperatures approaching absolute zero. This subject has been discussed by Rodebush (40). Certain of his conclusions are criticized in a forthcoming note by Pauling and Eastman (36). The features of interest here may be outlined as follows. Consider first a solution which is ideal at all temperatures. If such a solution be cooled to the neighborhood of absolute zero so slowly that it remains for times long compared with the time of transition between configurations at each temperature, its entropy of mixing will be lost, owing to the splitting of levels resulting from interaction of the various configurations. This will also be true on rapid cooling, provided the solution is finally held for a long time (compared to the time for transitions) at the low temperature. If such times be not allowed, the degeneracy of the system will not be lost and the entropy of mixing will remain. In the constrained systems, however, these long times are inconsistent with the constraints and cannot be considered, since the systems would go over, if transitions are occurring between configurations, to stable ones of zero entropy. In all cases of physical interest (real solutions and glasses, and ordinary times of observation) therefore, the predictions are in harmony with those deduced above from the older statistical considerations. The application of quantum mechanics nevertheless represents a real advance in interpretation.

THE PRINCIPLE OF THE UNATTAINABILITY OF THE ABSOLUTE ZERO

The relation of the "principle of unattainability" to the Nernst theorem and to the second law is outlined by Bennewitz (2), and shown not to be identical with either. The adoption of the views outlined above recognizing the existence of non-zero entropies or entropy changes in certain cases near the absolute zero denies the purely thermodynamic implications of the unattainability principle. This does not impair the truth of the principle, but places its validity upon a different basis, namely, the impossibility of carrying out experimentally isothermal processes involving certain types of constrained systems near absolute zero. This impossibility is perhaps more nearly related to fact than principle. In this case the fact is, of course, readily interpretable (43). This does not detract from the value or correctness of the idealized thermodynamic consideration of such processes. Nor is it justifiable to consider solid solutions and glasses as "non-thermodynamic" (44) phases, since in certain real processes their constraints can be maintained, and thermodynamics is directly applicable.

It may be noted here also that the unattainability theorem cannot be connected with the uncertainty principle as suggested by Rodebush (40). The latter principle in fact requires (36) the assignment of non-zero values of entropy to glasses and solutions under the circumstances discussed above, and is thus directly opposed, thermodynamically, to the former.

Apart from these considerations, the use of the unattainability theorem is generally but a clumsy alternative for more straightforward methods, and little of value is ever gained from it alone. Eastman and Milner (7) have suggested that it may well be dispensed with in thermodynamics.

ENTROPY AT HIGH PRESSURES

This question was first approached by Polányi (39) and later developed independently by Lewis (31), the conclusion of both authors being that at infinite pressures entropy becomes zero at finite temperatures. Lewis showed that the experimental behavior of the alkali metals appears to be in harmony with this idea. Bridgman (4) has recently pointed out, as a condition for this behavior, that the coefficient of thermal expansion must ultimately decrease at least as rapidly as $1/p$. He finds that for substances other than the alkali metals this is far from true at the highest pressures yet reached experimentally. Recognizing that experimentally attainable pressures are relatively small in the sense implied in this connection, and that a reversal in trend at higher pressures may occur, he nevertheless questions the necessity for the assumption of approach to zero entropy, suggesting that degrees of freedom previously frozen may become active at high pressures. It is, however, difficult to believe that the effect of increasing pressure will not ultimately lead to increasing separation of the energy levels of any system, with consequent continued decrease toward unity in the number of statistical distributions consistent with the temperature, and therefore to zero entropy. If however this occurs only outside the range of pressures that can be studied experimentally, the usefulness of the theorem is of course reduced.

STATEMENT AND NATURE OF THE THIRD LAW

There is one statement of the third law which meets with nearly universal agreement. Any phase cooled to the neighborhood of the absolute zero under conditions such that unconstrained thermodynamic equilibrium is attained at all stages of the process, approaches a state of zero entropy. This is, however, an unnecessarily restrictive form, since many constrained systems also approach zero entropy. The various formulations which attempt to include this fact have been briefly discussed by Eastman and Milner (7), who also propose the following inclusive and sufficiently restrictive statement; the entropy at the absolute zero of any phase of sharply specifiable energy is zero. In view of the general understanding which prevails, matters of statement are perhaps unimportant, except in so far as they emphasize significant features.

The statement of the third law in the form that entropy is a finite positive quantity, together with the rule of its approach toward zero with decreasing temperature or increasing pressure (31, 34), emphasizes its distinction in character from the other two laws. Each of the latter defines a thermodynamic quantity, while the third law merely limits one of these quantities. It differs essentially in type therefore from the first and second laws. Since it does not add to the content of the science its incorporation as one of its "laws" is of doubtful logic, although this usage seems to be established.

CONCLUSION

The evidence and arguments presented (very sketchily, indeed) in this review amply substantiate the central theorem under discussion. Its accurate application will always require discretion in consideration of the factors discussed here, as well as numerous points of a practical character. Moreover, the appropriateness of the usually accepted name is questionable. In spite of this, it seems not too much to say that neither the validity of the third law, its great utility, nor its continued importance since its inception in determining the course of the related sciences, can reasonably be denied.

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DISCUSSION

Dr. Rodebush. I do not disagree in any important detail with what Dr. Eastman has said, but I should like to add a few words as to my point of view. Eastman and Milner have stated that the low temperature states of mixed crystals and supercooled liquids are statistically indeterminate. Lewis and Gibson used the term "randomness" in this connection. If we understand by randomness the possibility of the existence of different configurations having the same energy then we can interpret the situation, but not without recourse to wave mechanics. According to wave mechanics a system behaves as though it were aware of the existence of other configurations having the same energy as the one in which it exists. This leads to a multiplicity of energy levels. If a system were in the lowest of these energy levels its entropy would be zero, but we can not know which level it is in because of the uncertainty principle. To determine the energy exactly would require so long a time that the system might not remain in its original state. This point of view is, therefore, in entire agreement with the statement of Eastman and Milner, that the low temperature state is statistically undefined.

Dr. Johnston. I think it unfortunate in some respects that the concept of zero or minimum entropy is so closely associated with that of minimum energy or that entropy increases are ordinarily associated with temperature increases. The relation between entropy and energy is an indirect one and exists because increase of thermal energy results, in practice, in an increased distribution of molecules among a wide number of discrete states. But it is the distribution, rather than the energies involved, which is the important thing. Thus if one could activate a gram-atom of mercury vapor *all* to the metastable $^3P_0$ state there would be no increase in entropy in spite of this large addition of energy. The fact that the system produced does not correspond to a stable one has, of course, nothing to do with the immediate value of the entropy. When this conception is applied to the situation which exists at or near the absolute zero it is apparent that disagreements with respect to the validity of the third law resolve themselves into disagreements in arbitrary definition.