

showed that 0.1% of an impurity may thus be detected with certainty. It may therefore be concluded that the element, if present, existed in smaller amounts.

Work on the problem is being continued.

The writer wishes to express his appreciation of the kindness of Professor B. S. Hopkins of the University of Illinois in furnishing the samples of rare earths, and of the assistance given by Professor H. S. Uhler and other members of the Department of Physics of Yale University.

### Summary

1. Spectroscopic evidence indicates that an element, probably number 61, may be associated with neodymium and samarium.
2. X-ray analysis of samples from different sources has so far given no evidence of the presence of this element.

NEW HAVEN, CONNECTICUT

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]  
**A STATEMENT OF THE THIRD LAW OF THERMODYNAMICS**

BY E. D. EASTMAN

RECEIVED OCTOBER 4, 1923

Lewis and Gibson<sup>1</sup> state the third law of thermodynamics as follows: "If the entropy of each element in some crystalline form be taken as zero at the absolute zero, the entropy of any pure crystal at the absolute zero is zero, and the entropy of any other substance is greater than zero." The essential features of this view are embodied in the more comprehensive statement of Lewis and Randall:<sup>2</sup> "Every substance has a finite positive entropy, but at the absolute zero of temperature the entropy may become zero, and does so become in the case of perfect crystalline substances." In seeking the theoretical basis of the law as stated above, Lewis and Gibson conclude that the entropy of a system in any state is associated with the randomness of that state, and that perfect crystals at the absolute zero lack any sort of randomness, while non-crystalline substances possess it. Some of the questions arising from these considerations have been experimentally investigated by Gibson, Parks and Latimer,<sup>3</sup> and by Gibson and Giaque.<sup>4</sup> The results obtained in their researches make it appear very probable that the entropy of supercooled liquids at the absolute zero is in fact greater, as predicted by Lewis and Gibson, than that of the corresponding crystalline substances. That the correct ex-

<sup>1</sup> Lewis and Gibson, *THIS JOURNAL*, **42**, 1529 (1920).

<sup>2</sup> Lewis and Randall, "Thermodynamics, and the Free Energy of Chemical Substances," McGraw-Hill Book Company, New York, 1923.

<sup>3</sup> Gibson, Parks and Latimer, *THIS JOURNAL*, **42**, 1542 (1920).

<sup>4</sup> Gibson and Giaque, *ibid.*, **45**, 93 (1923).

planation of their greater entropy is to be found in the greater randomness of state of the glasses, seems also very likely. Assuming this to be the case, reasons may nevertheless be advanced for believing that crystals themselves are random in character to varying degrees, and that the statement of the third law must be still further restricted.

In discussing this question it at once becomes desirable to establish some criterion of randomness. The measure of this quantity (or "quality") which it is proposed to use in the following argument is the number of atomic positions which it is necessary to specify in any system in order to define its state. On this basis, symmetry or regularity of arrangement reduces randomness, and irregularity increases randomness only in so far as they make the number of specifications required to reproduce the state smaller or larger. Whether other standards may be devised or not, the simplicity and generality of this statistical one commend its use and lend interest to the results of its application.

The relations and differences between crystals and glasses from the standpoint of their statistical definition become apparent from the following considerations. The crystalline state is characterized by the systematic repetition of some atomic grouping commonly called the "unit cell" of the crystal. To define completely a system in such a state it is necessary only to define the unit cell and specify the number of cells constituting the system. In substances which are mono-atomic in a crystalline sense the definition of the unit cell consists in the statement of the position and properties of each atom contained in it. When chemical molecules are involved the number of specifications may be cut down by giving positions of molecular centers and coordinates of each atom of the molecule referred to these centers. The particular manner of definition is, however, immaterial, provided the number of coordinates required to describe the unit cell is a minimum. In glasses nothing corresponds to the unit cell of crystals. It is, nevertheless, possible for the present purpose to consider another concept in an analogous role. Thus, on beginning with an element of volume enclosing only one atom in the glass, and continuously expanding its boundaries to enclose larger and larger numbers of atoms, a place will be reached where the inclusion of more atoms does not change the intensive properties of the enclosed medium. These limiting volumes may be regarded as the units from which the glass is constructed. They obviously differ from the unit cells of crystals, since no two of them would be precisely alike in atomic arrangement. They resemble unit cells in that they would all be (closely) alike in the number of specifications required to define them and alike in all their properties.

By the assumptions made above, the least number of atomic positions which must be specified in order to describe the unit cells of crystals or the unit elements of glasses fixes their randomness and their entropy. From

their definition and character the unit elements in glasses must contain large numbers of atoms or molecules and require many coördinates to define. In crystals of simple type, on the other hand, the unit cell is defined by relatively few specifications. As the complexity of the substance increases, however, this number may itself become quite large. Indeed, in the ideal case at least, there is no limit to the number of atoms per unit cell, nor to the irregularity of their configuration within the cell. Now, if various aggregates be considered in which the total number of atoms is the same in each, while the number per unit cell increases successively from case to case, a gradual transition from obviously ordered states to complete disorder—between crystal and glass—must, in the most general case, be observed. Crystals having one atom per unit cell and glasses then represent the limits between which substances may vary in randomness or any other property characteristic of state, and differ in this regard only in degree and not in kind. Complex crystals, therefore, possess finite entropy if glasses do.<sup>5</sup>

In the real crystals of common interest the number of atoms per unit cell is often small. This is probably true, for example, of every substance for which it has so far been possible to test the third law. It is not surprising, therefore, that among these crystals significant differences in entropy at the absolute zero have not been found experimentally. Whether appreciable amounts of entropy may be possessed by more complex (crystalline) substances is difficult to say in the absence of any clue as to the manner of dependence of entropy upon randomness as above defined. Attempts to estimate the approximate order of the effect are, nevertheless, not without interest. One such attempt will be discussed in the succeeding paragraph.

If the foregoing reasoning is correct, the entropy,  $S$ , is equal to the product of some function,  $f$ , of the number of atomic positions,  $m$ , defining the unit cell of the substance, and to the number of cells comprising the system. If  $N$  is the total number of atoms under consideration, and  $n$  the number of atoms per unit cell, the expression for entropy is therefore

$$S = \frac{N}{n} f(m) \quad (1)$$

What form the function,  $f$ , should take is, as stated, not apparent. But certain general requirements which it seems likely this function should meet can be named. Thus, for the simplest crystals with  $m = 1$ ,  $f(m)$

<sup>5</sup> It should be noted that this conclusion is a consequence of the argument that glasses and simple crystals are extremes in a series of states separated from one another by small gradations. Once this is recognized the conclusion is seen to depend only upon the assumption that glasses possess some entropy at the absolute zero, and not at all upon the definition of randomness, or even upon the cause to which the entropy is to be attributed. In the above, the development of this idea has been interlinked with the conception of randomness, partly for convenience in presentation, partly because of the high probability that randomness is the actual cause of the effect.

should probably be zero. Again, in order not to exaggerate the estimates for simple crystals,  $f(m)$  should perhaps be assumed to increase more rapidly than  $m$ , making the largest entropy effects per unit cell occur when  $m$  is large. A simple function which meets these requirements with sufficient exactness for the present purpose is

$$f(m) = c \ln m^m \quad (2)$$

where  $c$  is a constant, possibly, though not necessarily, a function of  $R$ . Equations 1 and 2 lead to

$$S = c N \frac{m}{n} \ln m \quad (3)$$

Equation 3 will serve,<sup>6</sup> it is thought, to show in a very rough way the order of the effects which may reasonably be expected. From the work of Gibson and Giauque<sup>4</sup> the entropy of glasses at the absolute zero may be of the order of 0.4 entropy unit per mean gram atom. It is probable also that for glasses  $m$  is of the order of  $n$ , and that  $10^{15}$  is a sufficiently large value to ascribe to either of these numbers. If so, the constant  $c$  in Equation 3 may be evaluated and used in calculations pertaining to crystals. As an illustration, a hypothetical substance<sup>7</sup> having 20 atoms per molecule and characterized by values of  $n$  and  $m$  of 400 and 100, respectively, will be used. For such a substance the calculated entropy is about 0.013 per mean gram atom, or 0.26 per molecule. Differences in entropy of this magnitude correspond at ordinary temperatures, to differences of 10–15% in the equilibrium constants of reactions involving one mol. As the chosen example is far from being the most complex type which may be met, it would seem that the entropy of some crystals at the absolute zero may be large enough to be of practical importance in accurate determinations of entropy from specific heats.

From the scientific as contrasted with the engineering point of view, the numerical magnitude of the effect, if it exists, is a matter of indifference. The important question is whether the third law is of as universal and exact validity as the other laws of thermodynamics. The argument which has been advanced here would place the current statements of it in somewhat the same position as the law of simple multiple proportions, since their force is diminished if departure is made from simple substances. However, if the conditions are in reality as they have been pictured here, a statement

<sup>6</sup> It is obvious but perhaps should be explicitly emphasized that this equation and the results to which its subsequent application lead, are purely suggestive in character and without exact significance. Their inclusion here is justified only because our knowledge in this field is at present so imperfect that every hint is valuable.

<sup>7</sup> The numbers in this illustration were chosen after consideration of sodium hydrogen acetate, which has 16 atoms per chemical molecule, and which is known [Wyckoff, *Am. J. Sci.*, **4**, 193 (1922)] to have 24 molecules or 384 atoms per unit cell. Its complete structure is not known, but if each molecule gives rise to 4 "crystal ions" as units of the lattice,  $m$  would appear to be of the order of 100.

of the third law can be made which is less open to this objection. For this purpose *it is necessary to recognize varying types of reactions in condensed systems, depending in any given case upon the number of specifications required to define the unit cells, in addition to the number of molecules, of each substance involved in the reaction.* The statement of the third law which it is desired to propose then is: *At the absolute zero entropy changes in all reactions of the same type are equal, and in reactions in which the system does not change in type entropy changes are zero.*

### Summary

The argument is made that there is in the ideal case no sharp dividing line between the crystalline and the (supercooled) liquid states. If the conclusion of Lewis and Gibson is accepted that glasses possess finite entropy at the absolute zero, it is necessary to believe that complicated crystals also do. Following Lewis and Gibson, randomness is regarded as the source of the entropy differences among glasses and crystals at the absolute zero, and the minimum number of atomic positions necessary to define the state of any system is adopted as a measure of its randomness. From the results of certain plausible assumptions as to the form of the relation between entropy and randomness, it appears possible that measurable entropy effects may be found in real crystals of the more complex types. Finally, a statement of the third law is proposed which is in harmony with these ideas.

BERKELEY, CALIFORNIA

---

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

## A RAPID METHOD FOR THE DETERMINATION OF HEATS OF ADSORPTION AND SOME VALUES FOR HYDROGEN ON NICKEL AND COPPER

BY RALPH ALONZO BEEBE AND HUGH STOTT TAYLOR

RECEIVED OCTOBER 19, 1923

In the course of investigations carried on in this Laboratory concerning the properties of metallic catalysts, it became desirable to obtain values for the heats of adsorption of various gases on those bodies. The case of hydrogen on nickel<sup>1</sup> was of particular interest and importance. A perusal of the literature revealed few of the data desired.

The first quantitative work of this kind was done by Favre,<sup>2</sup> although the thermal effect of adsorption had been observed by Mitscherlich<sup>3</sup> in his very excellent paper "Sur L'affinité Chimique." Favre, using a mercury calorimeter, obtained values for

<sup>1</sup> Gauger and Taylor, *THIS JOURNAL*, **45**, 920 (1923).

<sup>2</sup> Favre, *Ann. chim. phys.*, [5] **1**, 209 (1874).

<sup>3</sup> Mitscherlich, *ibid.*, [3] **7**, 18 (1843).