VOL. 42. AUGUST, 1920. No. 8.

THE JOURNAL

OF THE

American Chemical Society

with which has been incorporated the

American Chemical Journal
(Founded by Ira Remsen)

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE THIRD LAW OF THERMODYNAMICS AND THE ENTROPY OF SOLUTIONS AND OF LIQUIDS.

BY GILBERT N. LEWIS AND G. E. GIBSON.

Received April 9, 1920.

The third law of thermodynamics, as stated by Nernst, requires that the change in entropy accompanying any process, involving only solid and liquid substances, approaches zero as the absolute zero of temperature is approached. Planck[1] has shown, however, the necessity of modifying this statement when processes of solution are concerned. He pointed out the convenience of so choosing the arbitrary zero of entropy that the entropy of every elementary substance is zero at the absolute zero. With this convention, he states the third law as follows: the entropy of any pure substance is zero at the absolute zero.

In a recent article,[2] by comparing the results of equilibrium measurements with those obtained from the study of specific heats at low temperatures, we have brought forward a good deal of evidence for the validity of the third law, but the cases there cited involved only pure crystalline substances. Indeed there have been no experiments published hitherto which give any information regarding the thermal properties of solutions

---

[1] Planck, "Thermodynamik," 3rd Ed. 1911, p. 279.

[2] Lewis and Gibson, THIS JOURNAL, 39, 2554 (1917).

at low temperatures. There are, however, certain considerations of an *a priori* character which seem to us to justify the conclusion that some and perhaps all solutions are to be excluded in the statement of the third law.

When 2 liquids like benzene and toluene are mixed, they form approximately what is known as a perfect solution; that is, one in which there is no heat of mixing, and in which the vapor pressures or fugacities obey Raoult's law. The increase in entropy in producing one mol of the mixture from the 2 pure constituents is given by the equation

$$\Delta S = -N_2 R\, ln\, N_2 - N_2 R\, ln\, N_2 \qquad (1)$$

where N_2 is the mol fraction of the first and N_2 of the second constituent. For an equimolal mixture where $N_1 = N_2 = 0.5$,

$$\Delta S = R\, ln\, 2 = 1.4 \text{ cal. per degree.}$$

In such a case as this we find also that the heat capacity of the mixture is about equal to the sum of the heat capacities of the pure constituents, and, therefore, ΔS must be nearly independent of the temperature. For we have the thermodynamic relation

$$\frac{d(\Delta S)}{dT} = \frac{\Delta C_p}{T} \qquad (2)$$

where ΔC_p is the difference between the heat capacity of the solution and the heat capacity of the pure substances from which it was formed.

If now the solution and the 2 pure liquids can be cooled to very low temperatures without crystallization, as indeed can be done with many liquids owing to the phenomenon of supercooling, then if the solution continues to behave as a perfect solution (that is if ΔC_p remains zero), ΔS will remain constant and equal to $R\, ln\, 2$ down to the absolute zero. However, we know that many solutions which are nearly perfect at higher temperatures diverge in a pronounced manner from the behavior of the perfect solution at lower temperatures, and it is possible that at low temperatures the heat capacity of the mixture might become greater than that of its pure constituents, so as to reduce ΔS to a small value or even to zero at the absolute zero.

Nevertheless it would seem hardly likely that this phenomenon could occur in such a way as to reduce ΔS to zero in the limit for all types of solutions.[1] Thus with a mixture of 2 almost identical organic isomers we should expect ΔC_p to be nearly zero, and, therefore, ΔS to be nearly constant over a wide range of temperature. This reasonable surmise becomes a conviction when we consider the extreme case of a mixture of two isotopes. Here we have substances which are so nearly identical in prop-

---

[1] Planck indeed assumes that for all solutions Equation 1 holds at the absolute zero. There seems to be no evidence at present to support this assumption, and we shall, therefore, content ourselves with the proof that ΔS in a process of solution is not in general equal to zero at the absolute zero.

erties that as yet no way has been found for bringing about their separation. We even find isotopes which have not only the same atomic number but also the same atomic weight. It seems hardly conceivable that 2 such isotopes would suffer any measurable change in heat capacity on mixing, and, therefore, we must conclude that in such a case the entropy change on mixing remains essentially constant down to the absolute zero.[1]

We may, therefore, conclude that at the absolute zero there is in general a difference in entropy between a solution and the pure substances of which it is composed. In other words, if we assign zero entropy to the pure substances we cannot take the entropy of the solution as zero.

The Entropy of Pure Liquids.

The conclusion we have just reached, concerning the entropy of solutions, immediately raises a doubt as to the validity of the third law when applied to supercooled liquids or glasses, even when composed of a single constituent. The distinction between a pure liquid and a solution is in some measure artificial. Thus water is probably composed of several molecular species, including simple molecules, various types of associated molecules, together with hydrogen and hydroxide ions. Yet water is regarded as a pure substance, since at ordinary temperatures the establishment of equilibrium between these various types of molecules is so rapid that water, in the condition in which we know it, can be formed instantly from a single molecular species. This might not be the case, however, if we could cool water to a very low temperature where the several molecular species could behave as independent constituents of a mixture.

Just such a state of affairs is known in the case of sulfur. Liquid sulfur at high temperatures has entirely reproducible properties, but at lower temperatures it behaves like a mixture of 2 substances, S_λ and S_μ, which are only slowly transformable into one another. By rapid cooling, and treatment with carbon disulfide, it is possible to ascertain the amounts of the 2 species, since one is soluble and the other insoluble in this solvent. Insofar as the 2 species are not transformed into one another, they act as entirely independent substances. Thus when crystalline sulfur melts it produces pure liquid S_λ and the addition of S_μ lowers the melting point

---

[1] In fact one such solution has already been thoroughly investigated. Ordinary lead is known to be a mixture of isotopes, and yet its specific heat at low temperatures follows quantitatively the course that would be predicted from the behavior of other metals. It is true, in this case we are dealing with a solid solution or mixed crystal, but all that we have said hitherto applies equally well to solid and to liquid solutions. In order to give an idea of the numerical magnitude of the change in heat capacity on the mixing of equivalent amounts of 2 isotopes, which would be necessary in order to make $\Delta S = 0$ at the absolute zero, we may point out that in the case of lead at the point where $C_p = 3$ for the average of the pure isotopes, C_p for the mixture would have to be 3.8 cal. per degree.

just as any other solute would. Therefore, if S_λ and S_μ are mixed there must be a definite increase in entropy.

This liquid mixture is readily supercooled by sudden chilling. If we should study this material at low temperatures and also pure S_λ and S_μ in the supercooled liquid state we should undoubtedly find at least a part of this entropy change persisting down to the absolute zero. If then we assign zero entropy to the supercooled S_λ and S_μ we cannot assume zero entropy for the mixture. But this mixture would ordinarily be classed as a pure substance, and is in fact composed of a single element. These conditions which happen to have been observed in the case of sulfur may exist in many other liquids and glasses.

Even if a substance contain but a single molecular species, if it is in an "amorphous" state or in the state of a supercooled liquid, there seems at present no reason, theoretical or experimental, which forces us to believe that such a substance falls within the scope of the third law.

A Restatement of the Third Law of Thermodynamics.

When we turn to the consideration of crystalline solids we not only find numerous cases in which the third law has been verified experimentally, but we also see some *a priori* reasons for the existence of such a law, even though these reasons cannot at present be stated with all the lucidity that might be desired.

Since entropy is a quantity defined for the purpose of giving mathematical expression to the second law of thermodynamics, and since that law, from the standpoint of statistical mechanics, is essentially a consequence of the law of probability, it is natural to look for a relation between the entropy of a substance in a given state and the probability of the particular arrangement of molecules which determines that state. Essays in this direction by Boltzmann and more recently by Planck, important and suggestive as they have been, have not sufficed to show just what this relationship is. Nevertheless, it seems to us that if the entropy of a given state be regarded as in some sense a measure of the randomness of that state, the condition of a perfect crystal of a pure substance at the absolute zero is unique. In a solution there is a random distribution of several types of molecules. Even in a pure liquid or glass there is some randomness of arrangement. In any substance at a finite temperature there is a random distribution of energy among the individual molecules. But in the pure crystal at the absolute zero no randomness remains, for when the positions and the properties of a few molecules are fixed, the positions and properties of all other molecules are completely determined; thus when a few elements of the crystalline structure are known we may build up the whole crystal by a process of repetition.

It is this lack of any sort of randomness that we believe to be the theoretical basis for the conclusion that the entropy of a perfect crystal of a pure substance vanishes at the absolute zero.

We, therefore, 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.*

It seems likely, however, that the difference between the entropy of a pure substance in a crystalline state and in an amorphous state may, in many cases, prove to be very small.

BERKELEY, CALIF.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

ENTROPY CHANGES AT LOW TEMPERATURES. I. FORMIC ACID AND UREA. A TEST OF THE THIRD LAW OF THERMODYNAMICS.

BY G. E. GIBSON, W. M. LATIMER AND G. S. PARKS.

Received April 9, 1920.

The third law of thermodynamics, which states that the entropy of all pure crystalline substances at zero absolute temperature is zero,[1] offers a ready method for the determination of the free energy of compounds which cannot conveniently be investigated by determination of equilibrium or electromotive force. This is in general true of organic compounds. If the specific heats of a compound and of its elements at various temperatures are known, ΔS, the entropy of formation of the compound from its elements may be calculated. It is necessary then to know only the heat of formation ΔH in order to obtain the free energy ΔF from the relationship

$$\Delta F = \Delta H - T\Delta S \qquad (1)$$

The only organic compounds for which specific heat measurements at low temperatures have been made are benzene and oxalic acid, investigated by Nernst.[2] Calculation of the free energy of these compounds by the method indicated above, offers no check on the validity of the Third Law, since the free energies of these compounds have not been determined by other methods. From the equilibrium between water, carbon monoxide and formic acid, Branch[3] has calculated the free energy of formation of formic acid from its elements to be

$$\Delta F_{298} = -85,200 \text{ cal.}$$

From the work of Lewis and Burrows[4] on the equilibrium between am-

---

[1] The exact statement of the third law has been discussed in the preceding paper by Lewis and Gibson.

[2] Nernst, *Ann. Physik,* [4] 36, 395 (1911).

[3] Branch, THIS JOURNAL, 37, 2316 (1915).

[4] Lewis and Burrows, *ibid.,* 34, 1575 (1912).