

and it has been shown experimentally by Gibson and Giauque⁴ that glycerol in the form of a glass does, as a matter of fact, appear to have a greater entropy at the absolute zero than the same amount of glycerol in the crystalline form.

The purpose of the present article is to investigate the entropy of supercooled liquids at the absolute zero by the methods of statistical mechanics. We shall in this way obtain a more precise idea of the factors which can make the entropy of a supercooled liquid or glass greater than that of the corresponding crystal. Indeed, we shall be able to show that the excess entropy of a glass is related in a simple and definite manner to the properties of the glass when regarded as a quantum system with its degrees of freedom in the *next to the lowest quantum state*. Incidentally, we shall also show that different crystalline forms of a substance have the same entropy at the absolute zero, irrespective of the number of atoms in the unit of structure of the crystal, in contradiction to the suggestion recently made by Eastman⁵ that the entropy is greater, the larger the number of atoms in the unit cell.

Our method of determining the difference in entropy between the crystal and glass will be to calculate the entropy increase which results from a reversible evaporation of crystal, followed by reversible reduction of pressure and condensation into the glass. To perform the computation we shall need vapor-pressure formulas for the crystal and glass. We shall derive these vapor-pressure formulas with the help of statistical mechanics, and in carrying out the derivations shall employ the language and methods of Ehrenfest and Trkal.⁶ Our formula for the vapor pressure of the crystal will be in agreement with that given by these authors. The formula for the vapor pressure of a glass, however, will contain a new factor which has not previously been elucidated in a quantitative manner.

The γ -Weight $\{\gamma\}$ Corresponding to a Given State

In order to derive the desired vapor-pressure formulas we shall regard the state of a system of s degrees of freedom as represented by the position of a point in a $2s$ dimensional phase space (γ -space) corresponding to the s -coördinates $q_1 \dots q_s$ and s momenta $p_1 \dots p_s$, which determine the behavior of the system. We shall find it convenient to distinguish three types of degrees of freedom: (1) "fully excited" degrees of freedom such that the corresponding coördinates and momenta can be regarded as governed by the classical laws of motion, thus allowing the representative point to assume a continuous range of positions in the γ -space; (2) "partially excited" degrees of freedom such that the corresponding coördinates and

⁴ Gibson and Giauque, *THIS JOURNAL*, **45**, 93 (1923).

⁵ Eastman, *ibid.*, **46**, 39 (1924).

⁶ Ehrenfest and Trkal, *Proc. Amsterdam Akad.*, **23**, 162 (1920); *Ann. Physik*, **65**, 609 (1921).

momenta can assume only values belonging to some particular quantized state, thus restricting the representative point to particular hyper-surfaces in the space; (3) "frozen-in" degrees of freedom such that the corresponding coordinates and momenta are in the lowest possible quantum state and the representative point is correspondingly located in the γ -space.

In order to determine the probability of a given state of our system, we shall employ the concept of γ -weight, which will be denoted by the symbol $\{\gamma\}$. The γ -weight of a given state will be determined by moving the representative point in the γ -space through all positions which correspond to the state in question. In general, the point will move throughout continuous hyper-volumes corresponding to fully excited degrees of freedom and will assume locations on definite quantum hyper-surfaces corresponding to partially excited or frozen-in degrees of freedom. In the case of the fully excited degrees of freedom we shall assign a weight equal to the continuous hyper-volume generated in the γ -space by the representative point. In the case of the other degrees of freedom, which are affected by quantum restrictions, we shall assign to each quantum hyper-surface the volume in the γ -space which lies between it and the next higher quantum hyper-surface, thus introducing the weight h for each degree of freedom involved. The total γ -weight $\{\gamma\}$ is obtained by combining the separate weights thus obtained.

The γ -Weight of Vapor and Crystal at Very Low Temperatures

Let us now consider a system of volume V containing $X, Y, Z \dots$ atoms of different sorts, *all* combined in molecules of composition $\xi, \eta, \zeta \dots$ and mass M . Let N molecules be in the form of a vapor with potential energy $N\chi$ and N' condensed in the form of a *perfect* crystal with potential energy $N'\chi'$. Furthermore, let the temperature be low enough so that all rotations and oscillations of the vapor molecules, as well as all degrees of freedom in the crystal, can be regarded as frozen in. Consider, however, that the $3N$ degrees of freedom corresponding to the translations of the vapor molecules are fully excited. Finally, let the total energy of the system E lie in the range between E_0 and $E_0 + dE_0$. We can then write for the γ -weight of the above state of the system

$$\{\gamma\} = \frac{X! Y! Z!}{N! \sigma^N} h^{3(x+y+z)-3N} V^N \frac{(2\pi MK)^{3/2N} 3}{\Gamma\left(\frac{3}{2}N\right)} \frac{1}{2} NK^{-1} dE_0 \quad (1)$$

where σ is the symmetry factor for the molecule and K , the translational kinetic energy of the vapor molecules, is connected with the total energy E and the potential energies of crystal and vapor molecules by the equation

$$E = K + N\chi + N'\chi' \quad (2)$$

The method of obtaining the above expression for the γ -weight of the state of the system needs but little elucidation. Starting from an initial phase of the system which belongs to the state which we are considering,

we make the N vapor molecules pass through the total volume V and assume all linear velocities which are consistent with the kinetic energy K which is available. As a result of this operation, the representative point in our space generates a $6N$ dimensional hyper-volume which is given by the last terms in Equation 1, the term V^N arising from the translation of the molecules throughout the volume available, and the term $\frac{(2\pi MK)^{3/2N}}{\Gamma(\frac{3}{2}N)} \frac{3}{2} NK^{-1} dE_0$ being the volume of the hyper-spherical shell of

$3N$ dimensions which is determined by the restriction that the kinetic energy must lie in a range dE_0 in width. We then multiply by the factor $h^{3(X+Y+Z)-3N}$ in order to introduce the weight corresponding to the frozen-in degrees of freedom, and finally multiply by the factorial term $(X! Y! Z!)$ which gives the number of ways of permuting the atoms so as to obtain further equivalent phases starting from the original phase of the system. This factorial term, however, has to be divided by $N!$ since our translation of the molecules through the volume V has already included this number of permutations, and by σ^N since the interchange of symmetrically placed atoms in a given molecule would leave the molecule in the same rotational quantum state.

The Vapor Pressure of a Crystal at Very Low Temperatures

To determine the vapor pressure of the crystal we must now find what distribution of the molecules between crystal and vapor will lead to the maximum value of the γ -weight as given by Equation 1. Using for greater convenience the logarithm of the γ -weight, and varying with respect to the number of molecules in the vapor state, we obtain as the condition for a maximum

$$\delta \log \{\gamma\} = -\delta N \log \sigma - 3 \delta N \log h + \delta N \log V + \frac{3}{2} \delta N \log 2\pi MK + \frac{3}{2} N \delta N \frac{d \log K}{dN} - \frac{3}{2} \delta N \log \frac{3}{2} N = 0 \quad (3)$$

where certain approximations have been introduced which become negligible when N is very large. Introducing the obvious condition (see Equation 2)

$$\delta K = (\chi' - \chi) \delta N \quad (4)$$

giving the kinetic energy of the molecules the value which it must have at the high dilutions involved

$$K = \frac{3}{2} N kT \quad (5)$$

where k is the Boltzmann constant, and putting for the pressure of the vapor

$$p = \frac{N}{V} kT \quad (6)$$

it can be shown that Equation 3 reduces to

$$\log p = \frac{\chi' - \chi}{kT} + \frac{5}{2} \log kT + \frac{3}{2} \log \frac{2\pi M}{h^2} - \log \sigma \quad (7)$$

which is the desired expression for the vapor pressure of a perfect crystal at very low temperatures.

Number of Arrangements of Molecules in a Supercooled Liquid

Similar methods to the above can be used to determine the γ -weight of a system composed of N molecules of vapor and N' molecules of supercooled liquid. In this case, however, an exceedingly important difference arises when we consider the number of ways of arranging the molecules which make up the liquid phase.

In a perfect crystal having a given size, shape and orientation each molecule occupies a definite equilibrium position about which it will oscillate when the temperature is raised, and the total number of different exemplars of the crystal which can be obtained will be found by permutations of the atoms which do not involve any change in the equilibrium positions of the molecules. In the case of a supercooled liquid, however, especially one composed of complicated molecules, there may be a number of ways of fitting the molecules together and still obtaining a glass occupying the same space. Hence, in addition to the exemplars which can be formed from a given sample of the glass by permutations of the atoms, we must also consider rearrangements which involve a shifting of the actual positions occupied by molecules.

In determining the number of arrangements which involve a shift in the position of the molecules we must proceed, however, with some care. We are going to apply our considerations to a system which has all its degrees of freedom frozen-in, and shall in any case assign a weight equal to the area $h = \int \int dq dp$ to each degree of freedom. Hence, a shift in the position of a molecule which does not move it out of the limits already allowed to it as belonging to the lowest quantum state must not be counted. That such a possibility might arise may be seen from the trivial example furnished by the quantization of the motion of a ball rolling back and forth in a bowl with a flat bottom, which in the lowest quantum state could be anywhere on the flat surface, or of a dipole rotator which in a force-free field might have any orientation in the state of zero rotation. To avoid difficulties of this kind, let us consider the properties of the glass when its degrees of freedom corresponding to the coordinates which locate the positions of its molecules have been excited to the first quantum state. If rearrangements are then possible which involve shifts in the mean positions of the molecules, the number of such different arrangements must be contained in the expression for the γ -weight of the glass.

In the case of glasses made from complicated molecules, it would seem probable that such shifts would be possible. On the other hand, in the case of a liquid made from a simple monatomic substance, it might be impossible to obtain any condensed phase at the absolute zero having greater

possibilities of rearrangement than belong to a crystal. This latter would seem to be borne out by the fact that the entropy of liquid helium, at the lowest temperatures where measurements have been made, has already dropped to less than one entropy unit.

As to the number of arrangements involving shifts in the equilibrium positions of the molecules of the liquid, this will obviously be some function of the number of molecules N' in the liquid, and in the next section we shall show that in the cases to be considered the function must have the form $ca^{N'}$, where c and a are constants.

Vapor Pressure of a Supercooled Liquid

In accordance with the foregoing, we can obtain an expression for the γ -weight of a system containing N molecules of vapor and N' of supercooled liquid by multiplying the corresponding expression for the case of a crystal by the number of ways of arranging the liquid molecules as discussed in the preceding section. Referring to Equation 1 we thus obtain

$$\{\gamma\} = \frac{X! Y! Z!}{N! \sigma^N} h^{3(x+Y+z)} e^{-sN} \phi(N') V^N \frac{(2\pi MK)^{3/2} N^3}{\Gamma\left(\frac{3}{2}N\right)} \frac{3}{2} NK^{-1} dE_0 \quad (8)$$

where we have represented the number of such arrangements by $\phi(N')$.

Determining, just as in the case of the crystal, the conditions for a maximum value of the γ -weight, we can then obtain in analogy to Equation 7 the following expression for the vapor pressure of the glass

$$\log p = \frac{x' - x}{kT} + \frac{5}{2} \log kT + \frac{3}{2} \log \frac{2\pi M}{h^2} - \log \sigma - \frac{d \log \phi(N')}{dN'} \quad (9)$$

where the last term arises from the possibility for rearrangements of the molecules of the glass.

We can now, however, easily determine the nature of the unknown function occurring in this last term. Since we shall consider that we have taken a large enough sample of glass so that the vapor pressure is independent of the size of the sample, it is evident that the last term must be a constant independent of the number of molecules in the glass N' . Let us then write

$$\frac{d \log \phi(N')}{dN'} = \log a \quad (10)$$

where a is a constant. Integrating, we can obtain $\log \phi(N') = N' \log a + \text{const.}$, or

$$\phi(N') = c a^{N'} \quad (11)$$

where c is a constant. Substituting in (9) we obtain for the vapor pressure of a supercooled liquid

$$\log p = \frac{x' - x}{kT} + \frac{5}{2} \log kT + \frac{3}{2} \log \frac{2\pi M}{h^2} - \log \sigma - \log a \quad (12)$$

Our method of development also provides some measure of information as to the magnitudes that the quantity a can be expected to assume, and

hence some idea as to the probable differences in the entropies of crystals and glasses which we may expect to encounter. Equation 11 gives us an expression for the number of ways in which we can arrange the N' molecules of a glass and still obtain an exemplar of the glass. If we should increase the number of molecules by one, the number of such arrangements would become

$$\phi(N' + 1) = c a^{N'+1} = a \phi(N') \quad (13)$$

Hence, the quantity a may be regarded as the average number of ways in which a single molecule can be rearranged in the liquid. In accordance with our previous considerations, however, it is evident that these rearrangements must be drastic enough so that the new position of the molecule would also correspond to a rearrangement when the positional degrees of freedom of the molecules are excited to the next to the lowest quantum state, with the further condition that the new positions of the molecules could not be obtained by a mere permutation of atoms. On the basis of this interpretation, it is evident that a will be a small number which increases as the complexity of the molecules increases.

Difference in Entropy of Crystal and Glass

We may now use Equations 7 and 12 for the vapor pressure of crystal and glass to calculate the change in entropy when we pass from crystal to glass at temperatures near the absolute zero.

For convenience and in accordance with a familiar formulation of the third law of thermodynamics, let us take our starting point for entropy measurements such that the entropy of the crystal is zero at the extremely low temperature involved. Starting with the crystal let us then form by reversible evaporation one mole of vapor at the vapor pressure. The entropy of the gas thus formed will evidently be

$$S = A \left[\frac{\chi - \chi' + \frac{5}{2} kT}{T} \right] \quad (14)$$

where A is Avogadro's number. Changing now from the vapor pressure p as given by Equation 7 to unit pressure, we obtain

$$\Delta S = A k \log p = A \left[\frac{\chi' - \chi}{T} + \frac{5}{2} k \log T + \frac{3}{2} k \log \frac{2\pi M}{h^2} - \log \sigma \right]$$

which combined with (14) gives us

$$S = A \left[\frac{5}{2} k \log T + k \log \frac{(2\pi M)^{3/2} k^{5/2}}{h^3} + \frac{5}{2} k - \log \sigma \right] \quad (15)$$

which is, of course, the familiar Sackur⁷ expression for the entropy of a monatomic gas at temperature T and unit pressure with the constant terms as first correctly obtained by Tetrode.⁸

⁷ Sackur, *Ann. Physik*, **36**, 958 (1911); **40**, 67 (1913); *Nernst-Festschrift*, **1912**, p. 405.

⁸ Tetrode, *Ann. Physik*, **38**, 434 (1912); **39**, 255 (1912).

Continuing the process we may now change the pressure on the gas to the vapor pressure of the glass as given by (12) and then carry out a reversible condensation. These steps will be seen to involve the entropy change

$$\Delta S = -A \left[\frac{5}{2} k \log T + k \log \frac{(2 \pi M)^{3/2} k^{5/2}}{h^3} + \frac{5}{2} k - \log \sigma - k \log a \right] \quad (16)$$

which combined with (15) gives us

$$S = A k \log a = R \log a \quad (17)$$

as the desired expression for the entropy of one mole of a supercooled liquid or glass at the absolute zero. Remembering the interpretation of a given above, we see that the entropy of supercooled liquids at the absolute zero may be expected to vary from zero for simple molecules to a few calories per degree per mole for complicated molecules.

Some Points of Interest

Before leaving these matters it is of interest to note that our considerations afford no basis for ascribing greater entropy to crystals with a complicated unit of structure than to those having a simple unit. Provided there is only a single set of equilibrium positions for the atoms that make up the crystal, the entropy will be the same for different crystalline forms of the same substance.

In the case, however, of solid solutions where variability of composition is possible we may expect increased entropy owing to the possibilities of increased randomness of arrangement just as with liquid and gaseous solutions. Also, other special cases might arise where a greater degree of randomness would be possible than in pure, perfect crystals, but such cases could be given a special treatment and would cause no confusion.

It is also of interest to examine the entropy of a system containing a number of individual crystals placed and oriented at random. If the individual crystals are large enough so that we make no appreciable error in assuming all the degrees of freedom belonging to atoms in the crystals as frozen-in, and if reversible evaporation and recondensation to form again the original crystals are possible, then it is evident that we may also ascribe zero entropy to such a set of crystals.

In conclusion, there is a point in connection with the γ -weight of crystals and glasses as given by Equations 1 and 8 which will bear further elucidation. In setting up these expressions it might appear as if we had incorrectly neglected the possibility of rearranging the molecules of the crystal or glass so as to give different positions, shapes or orientations to the whole condensed phase. It should be noted, however, that we are going to apply our considerations to a calculation of the vapor pressure of a given crystal or glass, and hence are interested in the rearrangements that can be brought about by the evaporation and recondensation of a small portion

of the original crystal or liquid. Under these circumstances the position, shape and orientation of the condensed phase is maintained constant by the condition that most of it will not evaporate at all and, hence, determines the location of the phase as a whole. The matter might be made clearer if we regarded N' not as the total number of molecules in the condensed phase, but as the number of molecules in a layer on the surface of the phase taken of sufficient depth so that no change in the results would arise from an increase of depth.

Summary

In the foregoing article we have applied the methods of statistical mechanics to a determination of the entropy of crystals and supercooled glasses, and have reached the following conclusions.

1. The difference per mole in the entropy of a given substance at the absolute zero in the form of a glass and crystal can be given by an equation of the form $S_{\text{glass}} - S_{\text{crystal}} = R \log a$, where a is a small number increasing with the complexity of the molecule.

2. The exact nature of the quantity a is given by the equation, $\phi(N') = ca^{N'}$, which gives the number of ways in which we can arrange the mean positions of the N' molecules of a glass, when the degrees of freedom corresponding to the positional coördinates are excited to the first quantum state, excluding arrangements which could be obtained by a permutation of atoms.

3. The entropy of a perfect crystal at the absolute zero is not dependent on the complexity of the unit of crystal structure.

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THE ACTION OF SOME OXIDIZING AGENTS ON SULFITE. II

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RECEIVED MAY 18, 1925

PUBLISHED AUGUST 5, 1925

In a recent paper¹ the writer stated that he had repeated in part the work of Mayr and Peyfuss² on the oxidation of sulfite with nascent bromine from a known amount of bromate and an excess of bromide to the solution of which they added in order, the sulfite and hydrochloric acid. At that time the author found the oxidation to sulfite incomplete, and the presence of the bromide of little influence. These results have since been fully confirmed, and his later work shows further that sulfite may be accurately determined with bromate and a small fraction of its equivalence of iodide, or with the bromine set free by the action of known bromate on an excess of bromide.

¹ Hendrixson, *THIS JOURNAL*, **47**, 1319 (1925).

² Mayr and Peyfuss, *Z. anorg. Chem.*, **127**, 123 (1923).