Free Volume and Entropy in Condensed Systems I. General Principles. Fluctuation Entropy and Free Volume in Some Monatomic Crystals

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Free Volume and Entropy in Condensed Systems

I. General Principles. Fluctuation Entropy and Free Volume in Some Monatomic Crystals

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In a system of atoms whose motions are classically excited, the change in entropy in any isothermal process can be written $R \ln (V_{f2}/V_{f1})$ per mole, one such term for each kind of atom in the system. The free volume V_f used in this expression is the effective volume accessible to the centers of gravity of the atoms, corrected for fluctuation effects. Corresponding expressions can be written for the classical (translational or rotational) part of the motions of polyatomic molecules in real liquids and solids. In solids the free volume can be written $V_f = Nvf$, where v is a box, or cage, volume accessible to one particle, and f, the fluctuation factor, has a numerical value which depends on the way in which the box is defined. $R \ln f$ is a contribution to the entropy of the system, and the name "fluctuation entropy" is proposed for it. The fluctuation entropy includes what has been called "communal entropy" as well as a term due to the temperature variability of cell sizes. The free volume in a monatomic crystal can be determined from thermodynamic data, one convenient relationship being $P_{vap} = (RT/V_f) \exp(-\Delta H/RT)$. When this is applied to the data for the vapor pressures of the solids A, Kr, Xe, Mg, Zn, Cd, Hg, values of V_f are obtained which are about ½ percent of the volumes of the solids. The values of f found for these crystals support Rice's view that solids should display a rather large fluctuation entropy.

INTRODUCTION

ONE of the outstanding features of the scientific history of the past twenty years has been the growing up, so to speak, of statistical mechanics.[1] This was made possible by the development of the quantum mechanics, and, in its turn, provided methods and points of view from which it became possible to discuss many old problems with new precision. One of the developments which have ensued is the concerted attack which has been made, within the last seven or eight years, on the problems of the liquid state. Discussions of this attack, the different directions from which it is being made, and the kind of success which it has attained, have been given in several recent treatments,[2] in which extended bibliographies may be found. The current situation is that a rather good qualitative understanding of liquids is now at our disposal. Moreover, many special models have been proposed, which have made possible successful quantitative treatments of the cases for which they have been developed. There still does not exist, however, a picture which is at once general enough and precise enough to permit the discussion, within a single framework, of all of the data on liquids, and on solutions, which need explanation, and which should in principle be able to serve as ammunition in the attack.

In the attempt to obtain such a picture it seems that the idea of free volume[3] should play an important part, if properly developed and used. This is because it is, on the one hand, a pictorial idea, and, on the other, is capable of being brought into an exact relationship with thermodynamics.

The present paper and the two which follow constitute an essay in the elaboration and application of the free volume concept. It turns out that the application makes possible, among other things, the pictorial interpretation of certain entropy rules obtained empirically by Barclay and Butler,[4] Bell,[5] and others[6] as well as of certain

[1] Compare, for example the books by J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940) and R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (The Macmillan Company, New York, 1940) with that of R. C. Tolman, *Statistical Mechanics* (Chemical Catalog Company, New York, 1927).

[2] J. E. Mayer and M. G. Mayer, *Statistical Mechanics*, Chapter 14, particularly Section *l*; R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics*, Chapter VIII; G. Jaffe, Phys. Rev. **62**, 463 (1942); O. K. Rice, J. Chem. Phys. **12**, 1 (1944).

[3] See note 2, and papers by Eyring and his collaborators, e.g., H. Eyring and J. O. Hirschfelder, J. Phys. Chem. **41**, 249 (1937); J. F. Kincaid and H. Eyring, J. Chem. Phys. **6**, 620 (1938).

[4] I. M. Barclay and J. A. V. Butler, Trans. Faraday Soc. **34**, 1445 (1938).

[5] R. P. Bell, Trans. Faraday Soc. **33**, 496 (1937).

[6] E.g., M. G. Evans and M. Polanyi, Trans. Faraday Soc. **32**, 1333 (1936).

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departures of solutions from "regularity" in the Hildebrand[7] sense. The point of view which is developed also makes it possible to discuss the anomalies of aqueous solutions of non-polar substances, and finally, to draw some new conclusions from the numerical values of the entropies of hydration of ions. These should be of importance for future developments in electrolyte theory.

GENERAL CONSIDERATIONS

The way in which free volume has been introduced in previous work, and the precise implications of the definitions which have been offered, have differed from author to author, and sometimes, for the same author, from time to time.[8] Some of the definitions have been fundamentally equivalent to the one employed in this paper, but so far as the writer is aware, no previous discussion follows quite the same method of development as is used here. This consists first in establishing a correlation of very general validity between the free volume as defined by ΔS for an isothermal process, and one obtained from a physical picture. From a study of simple systems rules are obtained by which the "picture" free volume can always be made to equal the "thermodynamic" free volume. It is then possible to use experimentally determined entropy changes to draw rather detailed conclusions about the physical nature of the systems concerned. Of course, physical pictures are things which we make for ourselves, and their use is optional, not obligatory. This means, among other things, that free volume is an auxiliary concept, with only such meaning as is put into it by the definition adopted. It follows that any correct statement that can be made with it, or about it, must correspond to an equally good statement which does not involve free volume at all. This does not mean, however, that the concept is without value. On the contrary it can be used, and is used in these papers, to derive, and make pictorial, entropy relations which are otherwise difficult to arrive at or to understand.

DIATOMIC ASSOCIATIONS

As an introduction to some necessary ideas, we begin the discussion of the relation between free volume and entropy by considering a case for which explicit and rigorous expressions can be written for all the quantities of interest, namely the association of two atoms to form a diatomic molecule. Specifically, consider the entropy change per mole when two ideal monatomic gases X and Y unite at constant volume to form the ideal diatomic gas XY. For any ideal gas the entropy per mole is

$$S=R[\ln (Q/N)+T(d \ln Q/dT)+1]$$

where Q is the partition function, and N is Avogadro's number. Therefore

$$\Delta S=S_{XY}-S_X-S_Y$$

$$=R\left[\ln\left(\frac{NQ_{XY}}{Q_XQ_Y}\right)+T\frac{d}{dT}\left(\ln\frac{Q_{XY}}{Q_XQ_Y}\right)-1\right] \quad (1)$$

$$Q_X=Q_{iX}\frac{(2\pi m_XkT)^{\frac{3}{2}}}{h^3}V,$$

where Q_{iX} is the partition function of X corresponding to nuclear and electronic energies, m_X is the mass of an X atom, V is the volume of the reaction vessel, and the other symbols have their usual meaning. Correspondingly,

$$Q_Y=Q_{iY}\frac{(2\pi m_YkT)^{\frac{3}{2}}}{h^3}V.$$

We now make some assumptions, the importance of which will be discussed later. We assume that the temperature is high enough to justify using classical partition functions for the rotational and vibrational motions of XY. We also assume that the vibration of XY is simply harmonic, i.e., obeys the law

$$r-r_0=A \sin (2\pi\nu t+\varphi), \quad (2)$$

and that the amplitude A is very small compared with the equilibrium separation r_0. Here $\nu=(1/2\pi)(f/\mu)^{\frac{1}{2}}$, where f is the effective restoring force constant, and μ is the reduced mass, equal to

[7] J. H. Hildebrand, J. Am. Chem. Soc. 51, 66 (1929); or *Solubility* (Reinhold Publishing Corporation, New York, 1936), p. 65.

[8] E.g., O. K. Rice, J. Chem. Phys. 5, 353 (1937), where an "internal volume" is defined in terms of an entropy change; Eyring (see references in note 3) writes a partition function for a liquid where E is sometimes temperature-dependent and sometimes not.

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$(m_X m_Y)/(m_X+m_Y)$. φ is an unknown phase constant. Since X and Y are assumed not to be identical, the symmetry number of the XY molecule is 1 and

$$Q_{XY}=Q_{iXY}\frac{[2\pi(m_X+m_Y)kT]^{\frac{3}{2}}}{h^3}V\cdot\frac{8\pi^2IkT}{h^2}\cdot\frac{kT}{h\nu}. \quad (3)$$

Substituting for ν, and remembering that I, the moment of inertia, equals μr_0^2, we can rewrite (3)

$$Q_{XY}=Q_{iXY}\frac{[2\pi(m_X+m_Y)kT]^{\frac{3}{2}}}{h^3}\cdot\frac{[2\pi\mu kT]^{\frac{3}{2}}}{h^3}\cdot V\cdot 4\pi r_0^2\cdot 2\left(\frac{\pi kT}{2f}\right)^{\frac{1}{2}}. \quad (4)$$

Since $(m_X+m_Y)\mu=m_X m_Y$ we can obtain from (4)

$$\frac{Q_{XY}}{Q_X Q_Y}=\frac{Q_{iXY}}{Q_{iX}Q_{iY}}\cdot\frac{4\pi r_0^2\cdot 2\left(\frac{\pi kT}{2f}\right)^{\frac{1}{2}}}{V}. \quad (5)$$

The contribution of nuclear multiplicities to the quotient of Q_i's will be a factor of unity by a general theorem.[9] The contribution on account of electronic multiplicities will in general not be unity. We may call it F_e. It will be independent of temperature if the lowest energy for electronic excitation both of the molecule XY and of the atoms X and Y is large compared to kT, and we shall assume this to be the case. Then with (5) and (1)

$$\Delta S=R\left[\ln F_e+\ln\left\{\frac{N\cdot 4\pi r_0^2\cdot 2\left(\frac{\pi kT}{2f}\right)^{\frac{1}{2}}}{V}\right\}+\tfrac{1}{2}-1\right]. \quad (6)$$

We may assume, as usual, that on the average an XY molecule spends only a very small fraction of its time in collision with other molecules or atoms. Between collisions it will be vibrating according to the law (2) with an amplitude A. The energy of this vibrational state is given by $\epsilon=\frac{1}{2}fA^2$. The average value of A over an assembly in thermal equilibrium is given by

$$\bar{A}=\left(\int Ae^{-\epsilon/kT}dpdq\right)\Big/\left(\int e^{-\epsilon/kT}dpdq\right),$$

which may be evaluated without difficulty to give $\bar{A}=(\pi kT/2f)^{\frac{1}{2}}$. Since we have assumed $A\ll r_0$, and $r-r_0$ varies between $-A$ and $+A$ in any vibration,

$$4\pi r_0^2\cdot 2\bar{A}=4\pi r_0^2\cdot 2\left(\frac{\pi kT}{2f}\right)^{\frac{1}{2}}$$

is the average volume of the spherical shell about an X atom within which the Y atom partner is to be found, or *vice versa*. If we call this v, (6) becomes

$$\Delta S=R\left[\ln F_e+\ln\frac{Nv}{V}-\tfrac{1}{2}\right]. \quad (7)$$

Apart from the terms $R\ln F_e$ and $-\frac{1}{2}R$, we see that in the association reaction the entropy change is the same as would have been produced by the isothermal compression of one mole of Y, say, from the volume it occupied before reaction to the average volume it occupies after reaction, namely the average volume in the spherical shells around the X atoms. Each X, being the origin for locating a Y, can still be anywhere in V, so that the entropy change contains no contribution on account of the X's. It is of course immaterial which atom, X or Y, is taken as being at the center and which in the spherical shell. The important thing is that after reaction one mole of particles remains free to move in V, and one mole has been restricted to move in Nv. Nv is thus a free volume.

In spite of the fact that this type of calculation is not new,[10] we shall find it instructive to follow out its implications in detail, turning first to the meaning of the term $-\frac{1}{2}R$ in (7). The derivation shows that this is the sum of the $-R$ term in (1) and a $+\frac{1}{2}R$ which appeared in (6) from $T(d\ln\bar{A}/dT)$.

It is not difficult to recognize that the $-R$ is connected with what has been called the "communality"[2] of the volume V, and the "noncommunality" of the volume Nv. Communality

[9] J. E. Mayer and M. G. Mayer, footnote 1, Section 6g, pp. 135–138.

[10] Cf. for example, J. E. Mayer and M. G. Mayer, footnote 1, Section 9e, pp. 213–217.

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has meant different things to different people, and part of the purpose of this paper is to discuss its significance. We shall therefore find it useful, to begin with, to consider what meaning can be given to it in clear-cut cases such as this one. In the nature of things, an X describing a volume v about a given Y cannot move into a second volume v about another Y without exchanging partners, or "places," with a second X. Exchanges can take place, in principle, by dissociation and recombination, so that every one of the N elements v is accessible to each X (or Y if we wished to consider the X's as centers). However, not all v's are accessible to all X's independently. On the other hand, before reaction the whole of V is accessible to each X independently. A configuration, for example, in which all the X's are to be found in one corner of V is very unlikely, but is not excluded, and makes its contribution to the partition function.

This is the meaning of the statement that the volume V is communal, whereas Nv is not.

As will appear later, it is permissible to associate this difference in communality with the term $-R$ in ΔS. Such a convention is useful in providing a physical interpretation for this term. Specifically, it gives a meaning to absorbing the $-R$ into the free volume, writing $V_f=Nv/e$ for an effective free volume, corrected to account for communality effects.[11]

The term $+\frac{1}{2}R$ in (6) is caused by the temperature variability of the free volume. The partition function for the vibrational motion can be written

$$Q_v=\frac{kT}{h\nu}=\frac{(2\pi\mu kT)^{\frac{1}{2}}}{h}\cdot 2\bar{A}, \tag{8}$$

where it appears in the form corresponding to a quasi-translational motion in one dimension, with a "volume" $2\bar{A}$. For a real one-dimensional translation, the partition function is

$$Q_1=\frac{(2\pi mkT)^{\frac{1}{2}}}{h}l, \tag{9}$$

where l, the free length, or "volume" is an external parameter of the system, and is not temperature dependent. Physically this means that the length l available to any one particle is the same as is available to any other particle. This distinguishes l in (9) from $2\bar{A}$ in (8), for $\bar{A}$ is an average obtained from many A's, some large and some small. The variation between different A's may be regarded as a manifestation of the fluctuations which are characteristic of all systems in thermal equilibrium.

Mathematically, the temperature dependence of $\bar{A}$ makes a contribution to the entropy through the term $T(d\ln Q/dT)$ in the general statistical formula. Physically, the meaning of this extra entropy is to be found in the statement of Lewis:[12] "gain in entropy means loss of information." Strictly, for purposes of entropy interpretation, the idea of the volume of a gas has this meaning, and only this: when we have said that a molecule is in V we have stated accurately all that we know about its location. In the one-dimensional case, the entropy contains a term $R\ln l$, which means that we know the molecule is within a length of exactly l. In getting the entropy from (8) we obtain a term $R\ln(2\bar{A})$. But this as it stands tells more than we know, for it implies that each "particle" may be found in a length of exactly $2\bar{A}$, which is not true. To make it right we must say that on the average a "particle" is to be found in a length $2\bar{A}$, and, except on the average, we do not know how much larger or smaller the actual length is within which we must look for any individual "particle." This extra ignorance corresponds to extra entropy. How much extra entropy it corresponds to depends on what we know of the amount by which individual A's may differ from $\bar{A}$. The information we have on this, or the measure of our ignorance, is expressed in the proportionality between A and the square root of T. This leads, as shown above, to the term $+\frac{1}{2}R$ for the extra entropy. This term can also be incorporated into the effective free volume by multiplying the latter by $e^{\frac{1}{2}}$. This gives, for comparison with V, an effective free volume, corrected for communality and temperature dependence, $V_f=Nv/e^{\frac{1}{2}}$.

It remains to consider the term $R\ln F_e$. If more than one electronic state is involved for any

[11] This amounts to defining the free volume in a perfect gas as identical with the physical volume V. It would perhaps be more logical, but would be less convenient, to call the free volume in the gas Ve, and that in the "condensed" system Nv.

[12] G. N. Lewis, Science 71, 569 (1930).

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of the particles, and in particular if the electronic state of either atom, or of the molecule, is one in which there is a resultant angular momentum, appropriate terms must be added to the corresponding entropies.[13] We shall write the sum of these terms equal to zero. One special case which would give this is that in which the atoms are in ^1S states and the molecule is $^1\Sigma$. This is a very unlikely state of affairs for such a reaction as has been considered here. Our purpose, however, in discussing this reaction has been to establish a point of view for considering the condensation of a gas to a liquid or a solid. In such a process, changes in multiplicity of electronic states do not, in general, occur. We shall therefore omit the term $R \ln F_e$.

If the atoms X and Y happen to be identical, the treatment must be altered in two respects. First, in Q_{XY}, the symmetry number $\sigma(=2)$ must go into the denominator. Second, the factor V/N in the quotient Q/N, which occurs in the entropy expression, is only half as great for the atoms as for the molecule. The net result is to make

$$\Delta S = R\left[\ln\left(\frac{2Nv}{V}\right) - \tfrac{1}{2}\right] = R \ln \frac{2V_f}{V}. \quad (10)$$

Physically this corresponds to the fact that, since XX, XY, and YY are all the same, a given X can have as a partner not only any Y, but also any other X, making twice as many cells of volume v accessible to any bound atom.

We may sum up the results obtained thus far as follows: In the idealized reaction considered, at temperatures corresponding to classical excitation of all motions, the entropy change may be written in the form

$$\Delta S = R \ln \frac{V_f}{V}, \quad (11)$$

where V_f, the effective free volume of the bound atoms, equals the sum of the actual volumes of the cells in which these atoms are to be found, corrected for the effects of "communality" and of the variability of the cell sizes. Since the free volume of an atom in an ideal gas is the volume V, we may write

$$\Delta S = R \ln \frac{V_{f2}}{V_{f1}} \quad (12)$$

for the process.

[13] J. E. Mayer and M. G. Mayer, footnote 1, Section 6*i*, pp. 140–144.

A TRIATOMIC CONDENSATION

An exactly analogous calculation can be made for the reaction of three atoms X, Y, and Z to form a triatomic molecule XYZ. This can be carried through most easily in the special case of a linear triatomic molecule, with Y in the center, and with X and Z of equal mass and bound to Y so as to give equal restoring forces and equilibrium distances of separation from Y. CO_2, generalized to classical excitation of all the vibrations, is a case of this kind, and may be used as a model. We may omit symmetry considerations which arise due to the identity of the O atoms, having seen above that these produce no essential change in the things in which we are interested.

The calculations for this example have been carried through, using the necessary properties of and constants for the normal vibrations, which are again assumed to be of small amplitude, and simply harmonic. In order to outline the results, we let A_1 be the amplitude of the symmetrical mode, that in which the two oxygens move in and out symmetrically, the carbon remaining stationary. A_1 is defined in such a way that $r_{O-O} - r_{O-O} = A_1 \sin(2\pi\nu_1 t + \varphi_1)$. Likewise let A_2 be the amplitude of the unsymmetrical mode, that in which the C oscillates back and forth between the stationary oxygens, in the line joining them. Let A_y and A_z be the amplitudes for the bending modes, such that, for example, y, the distance through which the carbon is displaced in the Y direction out of the X axis (which contains the two oxygen atoms) is

$$y = A_y \sin(2\pi\nu_y t + \varphi_y),$$

a similar relation holding for z. Then it works out that ΔS for the association of the three atoms to form the molecule is given by

$$\Delta S = R \ln \left[\frac{4\pi r_{O-O}^2 \cdot 2\bar{A}_1 \cdot 2\bar{A}_2 \cdot 2\bar{A}_y \cdot 2\bar{A}_z \cdot N^2}{V^2}\right]. \quad (13)$$

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The nuclear and electronic terms have been ignored as before. The absence of a numerical term in R is caused by cancellation (see below).

If we let $4\pi r_{O-O}{}^2 \cdot 2\bar{A}_1 = v_O$ and $2\bar{A}_2 \cdot 2\bar{A}_y \cdot 2\bar{A}_z = v_C$ then (13) becomes

$$\Delta S = R \ln \frac{Nv_O}{V} + R \ln \frac{Nv_C}{V}. \qquad (14)$$

v_O is the average volume of a spherical shell about one oxygen atom within which the other oxygen can be located after reaction. If one oxygen is taken as origin, the symmetrical vibration will carry the other oxygen in and out, as in the case of the diatomic molecule. This same vibration will also carry the carbon in and out and the rotation will carry it around on a spherical surface, but this motion of the carbon must be ignored in the entropy picture, and does not appear in the mathematical expression for the entropy. This corresponds to the fact that, for any given location of the outer oxygen in its shell, the position of the carbon, so far as it is governed by the rotation and the symmetrical vibration, is fixed. All of our ignorance of the orientation of the molecule, and of its state in respect to the symmetrical vibration, has been taken account of, and must not be counted again. The uncertainty which remains is of the position of the carbon between the two oxygens now thought of as fixed. Of this, all we know is that its center lies somewhere in a cubical box whose extension in the O−O line averages $2\bar{A}_2$, and which extends sidewise out of this line in the Y and Z directions by amounts which average $\bar{A}_y$ and $\bar{A}_z$, respectively, in both positive and negative senses.

The absence of a numerical term in (13) and (14) is caused by the fact that one dimension of the oxygen shell varies proportionally to $T^{\frac{1}{2}}$, and all three dimensions of the carbon box have this variation. This corresponds to extra entropy of $4\times\frac{1}{2}R$, which exactly compensates the $-2R$ caused by loss of communality of volume by one oxygen and the carbon. The inequality of distribution of temperature-variation entropy makes (14) deceptive, as it stands. To obtain effective free volumes for the C and O atoms which correspond correctly to the representation we have given of the CO_2 molecule, we must write

$$\Delta S = R \ln \frac{Nv_O}{Ve^{\frac{1}{2}}} + R \ln \frac{Nv_C e^{\frac{1}{2}}}{V} = R \ln \frac{V_{fO}}{V} + R \ln \frac{V_{fC}}{V}, \qquad (15)$$

that is, on our representation, V_f for the oxygen is smaller and V_f for the carbon is larger by a factor $e^{\frac{1}{2}}$ than N times the corresponding cell volume.

To complete the discussion of this special case we must now point out that while the foregoing treatment is consistent, and will give the correct value for ΔS, it is not unique. We could equally well have represented the CO_2 molecule as having the C atom free to move anywhere in V, with the two O atoms confined, respectively, to a spherical shell and a rectangular box. The result of this break-down is just as neat as the one in (15). It reads

$$\Delta S = R \ln \frac{V_{fo'}}{V} + R \ln \frac{V_{fo''}}{V}. \qquad (15')$$

If $V_{fO'}$ and $V_{fO''}$ are correctly evaluated (they will both be different from V_{fO} in (15)) ΔS will, of course, come out with the same value as before. The important point which this illustrates, and which we shall meet again later, is that we must not take too seriously the names by which it may be convenient to call individual contributions to an over-all entropy, or entropy change. Different ways of "taking apart" a given process may be useful for different purposes. They will all be equally "good" if they are carried through consistently and without error.

A GENERAL THEOREM

The cases which have been considered in detail above are of idealized molecules, and it is therefore important to recognize that they are examples of a theorem which is completely general so long only as all the motions involved are classically excited. This follows from the statistical definition of entropy as

$$S = k \ln \Omega, \qquad (16)^{14}$$

where Ω is the total number of possible states of

[14] J. E. Mayer and M. G. Mayer, footnote 1, Chapter 4.

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the system compatible with the prescribed total energy. Where the motions are classical, Ω is the volume of phase space within which the representative point for the system may be without violating the assumed conditions. That is

$$\Omega=\frac{1}{N_1!N_2!\cdots N_s!h^{3t}}\times\int^{\text{accessible region}}\cdots\int dp_1\cdots dq_t. \quad (17)$$

$N_1\cdot N_2$, etc., are the numbers of the different kinds of atoms present, and $3t$ is the total number of degrees of freedom of the system, since t is defined as $N_1+N_2+\cdots+N_s$. The divisions by $N!$ and by h^{3t} take care, respectively, of the indistinguishability of the atoms and the scale in which the phase volume is to be measured.[15] It is an important property of this integral[14] that the same numerical result for its logarithm is obtained whether the integration is extended (a) over the states corresponding to the most probable distribution of energy for total energy in the range E to $E+dE$, (b) over all states in which the energy of the system lies within the range E to $E+dE$, or (c) over all states in which the energy of the system is equal to or less than E. If changes of the system in respect to nuclear spin orientation or of electronic state were of interest, a factor Ω_i, could be multiplied into the phase volume. For reasons already mentioned, we omit this.

For our purposes we may choose as the q's in (17) the Cartesian coordinates of the individual atoms, x_1, y_1, z_1, $x_2\cdots$, the p's being the components of momentum p_{x1}, p_{y1}, etc. Then the energy E is

$$E_q+E_{\text{int}}+\sum_{i=1}^{i=t}\frac{1}{2m_i}(p_{x_i}^2+p_{y_i}^2+p_{z_i}^2),$$

where E_q is the potential energy, a function of the instantaneous positions of all the atoms, and E_{int} is the sum of the internal energies of all the particles. By the principle of equipartition of energy[16] the sum of the p^2 terms is $\frac{3}{2}tkT$, which will be correct for any state of the system in which all the external motions of the atoms are classical. The integral over the p's in (17), therefore, is the hypervolume of the hyperellipsoid which is defined by

$$\sum_{i=1}^{i=t}\frac{1}{2m_i}(p_{x_i}^2+p_{y_i}^2+p_{z_i}^2)=\tfrac{3}{2}tkT.$$

This hypervolume is equal to

$$\prod_{j=1}^{j=s}(2\pi m_jkTe)^{3N_j/2}$$

(s = number of kinds of atoms present),

which makes

$$\Omega=\prod_{j=1}^{j=s}\frac{(2\pi m_jkTe)^{3N_j/2}}{N_j!h^{3N_j}}\times\int^{\text{all } x,\ y,\ z\text{ compatible with } E}\cdots\int dx_1\cdots dz_{N_s} \quad (18)$$

$$=\prod_{j=1}^{j=s}\frac{(2\pi m_jkTe)^{3N_j/2}}{N_j!h^{3N_j}}V_{fj}^{N_j}, \quad (19)$$

where $V_{f1}=\int dx_1dy_1dz_1$ (over all configurations compatible with E), etc.

(19) may be taken as defining the free volume of any atomic species as the geometrical mean (i.e., the N_jth root of the product) of the extensions of real space accessible to each of the N_j atoms of the kind in question, taken with due regard to compatibility of these extensions with each other and with the volumes accessible to all the atoms of other kinds.

The theorem which follows from (19) is that for any isothermal change of the system

$$\Delta S=S_B-S_A=k\ln\frac{\Omega_B}{\Omega_A}$$

$$=N_1k\ln\left(\frac{V_{fB}}{V_{fA}}\right)_1+N_2k\ln\left(\frac{V_{fB}}{V_{fA}}\right)_2+\cdots, \quad (20)$$

or, per mole of each kind of atom, ΔS has a contribution R times the natural logarithm of the ratio of its free volume after the change to that before. This is a direct consequence of the equipartition of energy, which makes the factors preceding the V_f's in (19) cancel out if the temperature is held constant.

[15] J. E. Mayer and M. G. Mayer, footnote 1, Chapter 2.
[16] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics*, Section 332, pp. 121–123.

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For the special case of a perfect gas, $V_f = V$, and for a mixture of perfect monatomic gases (19) gives for each constituent a factor of

$$\Omega_g = \frac{(2\pi mkTe)^{3N/2}}{N!h^{3N}} V^N \tag{21}$$

in Ω or a molal entropy of

$$k \ln \Omega_g = R\left[\ln \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \cdot \frac{V}{N} + \frac{5}{2}\right]$$

as it must.

For the special case of a diatomic molecule such as the molecule XY considered to begin with, the evaluation of Ω is more conveniently carried out in terms of Cartesian coordinates for the center of gravity of the molecule, and polar coordinates for the relative positions of the atoms. The transformation to these coordinates involves introduction of reduced masses, and also gives momenta in such a form that E_p contains the coordinates also, e.g.,

$$\epsilon_{p_1} = \frac{p_{r_1}^2}{2\mu_1} + \frac{p_{\theta_1}^2}{2\mu_1 r_1^2} + \frac{p_{\varphi_1}^2}{2\mu_1 r_1^2 \sin^2 \theta_1}. \tag{22}$$

This results in an expression for Ω which does not lend itself in the intermediate stages to separation in such a form as (18). However, (19) is still correct for expressing the final value of the integral, which is

$$\Omega = \frac{(2\pi m_x kTe)^{3N/2}(2\pi m_y kTe)^{3N/2} e^{N/2}}{N!h^{6N}} \times V^N \left[4\pi r_0^2 \cdot 2\left(\frac{\pi kT}{2f}\right)^{\frac{1}{2}}\right]^N. \tag{23}$$

(23) with (21) gives

$$\frac{\Omega_{XY}}{\Omega_X \Omega_Y} = \frac{N!\left[4\pi r_0^2 \cdot 2\left(\frac{\pi kT}{2f}\right)^{\frac{1}{2}}\right]^N e^{N/2}}{V^N}, \tag{24}$$

or

$$\Delta S = k \ln \frac{\Omega_{XY}}{\Omega_X \Omega_Y} = R\left[\ln\left(\frac{Nv}{V}\right) - \tfrac{1}{2}\right] \tag{25}$$

as before (Cf. (6)), using v again for the volume of the spherical shell.

The existence of this general theorem shows that of all the restrictive assumptions made in obtaining Eqs. (2)–(7), and (13)–(15), the only essential one was that of classical excitation of the motions. If the vibrations had not been assumed small, nor harmonic, the mathematics would have become enormously more complicated, but a result of the same form (20), with the same physical meaning of V_f, must still have been obtainable in principle.

Since there are very few systems of physical interest in which all of the motions are classically excited, it is important to note that all of the results of this section hold for any classical part of the motion of a system if the remaining motions, classical or non-classical, can be assumed to be separable from the motion of interest, and not to change during the process under discussion. For Ω, as a total number of states, can be represented as a product of numbers of "sub-states" for the various modes of motion in which the energy is separable. In particular, for the external (translation) and internal (electronic, rotation, vibration, and internal rotation) motions of a system of molecules, Ω may be written

$$\Omega = \Omega_e \cdot \Omega_i. \tag{26}$$

Then if in a change from state A to state B, Ω_i is unchanged,

$$\Omega_B/\Omega_A = \Omega_{eB}/\Omega_{eA}. \tag{27}$$

Since the external motions of the molecules in gases and liquids can be taken as classical, it is therefore always permissible to write

$$\Delta S = R \ln \frac{V_{fB}}{V_{fA}} \tag{28}$$

for the part of the entropy change associated with motions of the molecular centers of gravity, so long as these are separable from the internal motions. We have shown that the free volumes suitable for use in (28) are real physical volumes which can be interpreted in terms of a physical picture. We have also shown, however, that the physical picture must be sufficiently refined to include a correct interpretation of communality and of the temperature dependence of cell volumes.

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POLYATOMIC LIQUIDS

Since we shall want, in the following paper, to use (28) in discussing the entropy change which accompanies the condensation of a gas to a liquid, we may pause here to consider how nearly this process fulfills the conditions of validity of (28), and what can be done in cases where it does not. We shall see later that in most real liquids the internal motions are not, in fact, as free as in their vapors. As it stands, therefore, (28) will not give ΔS of condensation correctly. However, the method used to derive (28) also provides a means of generalizing it, since in a number of important cases the significant interference with internal motions concerns rotation only. This follows from the fact that the positions of Raman lines and infra-red bands are not greatly changed in passing from the vapor to the liquid state, which means that the vibrations are, to a good approximation, not changed in frequency, or that the vibrational motions are not greatly perturbed. The broadening of the lines, or of the bands, on condensation is caused entirely by changes in the rotational energy differences which add to, or subtract from, the changes in vibrational energies which are being measured.

Now for all ordinary polyatomic molecules, the rotational motion is effectively classical. Therefore, proceeding along lines suggested by the pseudo-CO_2 case above, we can make a generalized Ω, and obtain a "complete" free volume for carbon tetrachloride, for example, which consists of the "ordinary" free volume of the molecular center of gravity, multiplied by the volume of the spherical shell containing one of the chlorine atoms, by a ring volume for a second chlorine, and by a box volume for each of the other two chlorines. The effective thickness of the spherical shell and the effective linear dimensions of the other volumes cannot be obtained by the methods so far employed, for the vibrational motions which determine them are not classical. This is of no importance for our purpose, however, as these non-classical quantities may be assumed, as just stated, to be unchanged by the condensation process, and will cancel out. The volume of the spherical shell, for CCl_4 vapor, is $4\pi r_0^2\Delta r$ as before, Δr being the effective thickness provided by the (quantized) breathing mode of vibration. The volume of the ring or "doughnut" is $2\pi r_0 \sin\theta wt$ where w is the effective width and t the effective thickness, determined, respectively, by specified bending and unsymmetrical valence vibrations. θ is the (constant) tetrahedral angle which determines the equilibrium inclination between the valence bonds from the carbon to the shell and ring chlorines. Then $4\pi r_0^2\Delta r \cdot 2\pi r_0 \sin\theta wtb_1b_2$ is the supplementary free volume which is to be multiplied into the ordinary free volume of the center of gravity to make the complete free volume, b_1 and b_2 being the effective volumes of the boxes occupied by the other chlorines.

When condensation takes place, and the rotation is no longer free, the chlorine which was chosen to move in the shell is now confined, on the average, to a restricted area on its surface, an area measured by s, the solid angle it subtends at the carbon center. The chlorine which was chosen to move in the ring is, at the same time, confined, on the average, to a restricted segment of it, a segment measured by the angle a it subtends at the planar center of the ring. The supplementary free volume is thus reduced to $sar_0^3 \sin\theta wt\Delta rb_1b_2$, all the factors except s and a being unchanged.

(28) is therefore generalized to

$$\Delta S = R \ln \frac{V_{fl} sar_0^3 \sin\theta \Delta rwtb_1b_2}{V_{fg} 8\pi^2 r_0^3 \sin\theta \Delta rwtb_1b_2} = R \ln \frac{\gamma V_{fl}}{V_{fg}}, \quad (28')$$

where V_{fl} and V_{fg} have the same meanings as before. γ equals $sa/8\pi^2$ and is the "free angle ratio" of Kincaid and Eyring.[17] It is the average fraction of the total free rotational motion which the molecule is still able to execute after condensation. It is clear that $\gamma \leqslant 1$.* The fact that the symmetry number of CCl_4 is 12 affects both numerator and denominator of γ in the same way, and means, merely, that the 12 equivalent positions in which a CCl_4 can be caught by a snapshot of its rotation in the gas, or in which it can oscillate against its neighbors in the liquid, count as one only.

(28′) is rigorous, with the physical meaning we have given, so long, and in so far as, (a) the internal vibrational motions are actually separable from the translation and rotation of the molecule, (b) the internal vibrational motions of the molecule are not changed by the presence of neighbors, and (c) the oscillations which have replaced rotation in the liquid are effectively classical. It is probable that none of these conditions is exactly fulfilled, but it is also probable that none of them fails badly enough to discourage the use of (28′) for CCl_4. CCl_4, however, is an especially favorable case among real liquids. A treatment corresponding to that just given can of course be written down for any polyatomic liquid. But for long chain molecules, such, for example, as *n*-octane, it is likely that some intramolecular bending and torsional vibrations will interact with the translational and rotational vibrations of the whole molecule in the liquid in such a way that it will be impossible to calculate, or even to visualize separately, γ and V_f, as they appear in (28′). Formally (28′) will still mean what it purports to if the product γV_f is considered as a single quantity. But the treatment used later on, in which V_f for a liquid is calculated separately from a cell or cage model, will lose its clarity of outline in proportion as this difficulty becomes more acute.

Before attempting a complete analysis of so complicated a system as a polyatomic liquid, it will be necessary to explore additional simple cases upon which we may base a point of view and method.

COMMUNALITY IN A ONE-DIMENSIONAL SYSTEM

A model of a hard-sphere one-dimensional gas has been considered by Tonks,[18] and an analysis

[17] J. F. Kincaid and H. Eyring, J. Chem. Phys. 6, 620 (1938).

* The effective γ will presumably be larger than the geometrical picture would suggest, due to the effect of fluctuations.

[18] L. Tonks, Phys. Rev. 50, 955 (1936).

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of the small vibrations of a one-dimensional crystal suitable for our purposes is given by Mayer and Mayer.[19] The utility of these treatments in discussing communal entropy has been pointed out by Rice.[20] We shall repeat some of Rice's calculations, but shall arrive at results somewhat divergent from his.

Tonks[18] in effect evaluates the configuration integral for a one-dimensional gas of N molecules of a "hard" diameter σ, confined in a length l. It is assumed that when two molecular centers are farther apart than σ no force operates between the molecules. His result, for very large N, is

$$I=\frac{1}{N!}[l(1-\theta)]^N, \tag{29}$$

where θ is the fraction of the length occupied by the molecular diameters or $\theta=N\sigma/l$. This can be made into a classical (not yet normalized) phase integral, by multiplying by the momentum integral $(2\pi mkT)^{N/2}$, giving

$$Q'=\frac{(2\pi mkT)^{N/2}}{N!}[l(1-\theta)]^N. \tag{30}$$

The $N!$ in the denominator arises mathematically from the successive integration N times of an xdx in the configuration integral. Tonks points out that corresponding to the $N!$ serial orders in which N molecules, assumed to be distinguishable, can be arranged in line there are actually $N!$ equivalent regions of configuration space, of which (29) represents integration over only one. He justifies the restriction to one region by the fact that in a one-dimensional gas the molecules are unable to pass each other. This leads to the right result, but we wish to approach it differently. If Tonks' result is to be used physically it must lead to a partition function for a phase which could stand in equilibrium with other phases, so that "evaporation" and "recondensation" would enable any order to be realized, still imagining the particles to be distinguishable. The physical possibility or impossibility of interchanges in the linear gas is therefore irrelevant.[21]

To obtain the correct phase integral for the assumed system we must therefore multiply (30) by $N!$ before normalization. Normalization, in Boltzmann statistics, consists in dividing by h^N for unit of "volume" in phase space, and by $N!$ for the indistinguishability of the molecules,[15] and yields the correct partition function for the assembly as a whole

$$Q=\frac{(2\pi mkT)^{N/2}}{N!h^N}[l(1-\theta)]^N, \tag{31}$$

in agreement with Rice and, mathematically, with Tonks. As θ approaches zero, this approaches

$$Q=\frac{(2\pi mkT)^{N/2}}{N!h^N}l^N \tag{32}$$

in exact analogy with the expression for a perfect (three-dimensional) gas as a whole:

$$Q=\frac{(2\pi mkT)^{3N/2}}{N!h^{3N}}V^N. \tag{33}$$

The molal entropies corresponding to (31), (32), and (33) are given by the general formula

$$S=k\left[\ln Q+T\frac{d\ln Q}{dT}\right],$$

or, for (31)

$$S=R\left[\ln\frac{(2\pi mkT)^{\frac{1}{2}}}{h}+\tfrac{1}{2}+\ln\frac{l(1-\theta)}{N}+1\right], \tag{34}$$

and for (33)

$$S=R\left[\ln\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3}+\tfrac{3}{2}+\ln\frac{V}{N}+1\right]. \tag{35}$$

In each of these cases, the formula has been arranged so that there is a volume contribution to the entropy corresponding to a cell volume,

$$R\ln(V/N) \quad \text{or} \quad R\ln[l(1-\theta)/N],$$

plus an R which comes from the Stirling approximation for $N!$. As we have seen this is commonly called a communal entropy, and associated with the volume contribution. Logically it occurs along with $\ln N$ and is associated with V only as we choose to consider V and N together as the ratio V/N. From this point of view, the suggestion of

[19] J. E. Mayer and M. G. Mayer, footenote 1, Section 11*f*, pp. 246–248.
[20] O. K. Rice, J. Chem. Phys. **12**, 1 (1944).
[21] Cf. E. D. Eastman and R. T. Milner, J. Chem. Phys. **1**, 444 (1933).

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Rice[20] that a three-dimensional solid or liquid constructed in analogy with Tonks' one-dimensional gas or liquid should have a communal entropy of $3R$ is seen not to be correct. For the analog of (31) becomes

$$Q=\frac{(2\pi mkT)^{3N/2}}{N!h^{3N}}[l(1-\theta)]^{3N}, \tag{36}$$

the $N!$ appearing to the first power as before, this being the necessary and sufficient way of accounting for the indistinguishability of the N molecules present.[15] This gives

$$S=R\left[\ln\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3}+\tfrac{3}{2}+\ln\frac{[l(1-\theta)]^3}{N}+1\right], \tag{37}$$

as the superficially straight-forward generalization of (34) to three dimensions. Results obtained below suggest, however, that a straight-forward theoretical treatment of the 3-dimensional hard-sphere problem cannot be attained so simply except where θ is very small. Physically, the results for real crystals support Rice's idea that solids should have rather large amounts of entropy which may be called communal.

THE LINEAR CRYSTAL

The case of the linear monatomic crystal treated by Mayer and Mayer differs from Tonks' problem in that here the atoms of the crystal are bound to each other so that any displacement of one of them produces a force on its neighbors. The minimum of potential energy is assumed to correspond to equal separations of a units between all pairs of neighbors. The length of the crystal is thus $(N-1)a$ for N atoms. The displacement of the i'th atom is called ξ_i, and for small vibrations

$$E=E_0+\tfrac{1}{2}f\sum_{i=1}^{N-1}(\xi_{i+1}-\xi_i)^2.$$

For N very large, and the two end atoms assumed to be held fixed, it is shown that there are $N-2$ normal modes, such that the frequency of the n'th is

$$\nu_n=\frac{1}{\pi}\left(\frac{f}{m}\right)^{\frac{1}{2}}\sin\frac{\pi n}{2(N-1)}\quad 1\leqslant n\leqslant(N-2), \tag{38}$$

$m=$ mass of one atom. Since N is very large, this makes $\nu_{\max}$, the highest possible frequency, (sensibly ν_N)

$$\nu_N=(1/\pi)(f/m)^{\frac{1}{2}}. \tag{39}$$

This is easily shown to correspond to the mode in which neighboring atoms vibrate "against" each other, such that $-\xi_i=\xi_{i+1}=\xi_{i-1}$. The motion is described by $\xi_i=\pm A_N\sin(2\pi\nu_N t+\varphi)$, + sign for odd i, − sign for even i, i.e., the amplitude constant for the mode also describes the separate harmonic motion of each atom.

The method employed in the discussion following (6) can be used to obtain the average value of A_N in classical thermal equilibrium, and yields $\bar{A}_N=\frac{1}{2}(\pi kT/2Nf)^{\frac{1}{2}}$. The appearance of N in the denominator makes $\bar{A}_N$ a very small length even on an atomic scale. It is therefore of greater interest to consider another length, the average amplitude within which the atoms would vibrate if only this mode were excited, but the average energy of the crystal were NkT— i.e., if all of its actual equilibrium energy were concentrated in this one mode of highest frequency. This supposition corresponds to picturing the crystal as a sort of specialized Einstein solid, in which all of the virtual oscillators not only have the same frequency, but are reinforcements of a single actual normal mode of the crystal. The average value of A_N for such excitation may be called $\bar{A}_E$, and is given by

$$\bar{A}_E=\tfrac{1}{2}(\pi kT/2f)^{\frac{1}{2}}. \tag{40}$$

The partition function (classical) for the crystal is

$$Q=\prod_{n=1}^{N-2}(kT/h\nu_n), \tag{41}$$

so that

$$\ln Q=\sum_{n=1}^{N-2}\ln\frac{kT}{h\nu_n}$$

$$=N\ln\frac{kT}{h}-\int_0^N\ln\nu_n dn, \text{ sensibly.} \tag{42}$$

Integration gives

$$\ln Q=N\ln\left[\frac{(2\pi mkT)^{\frac{1}{2}}}{h}2\left(\frac{\pi kT}{2f}\right)^{\frac{1}{2}}\right] \tag{43}$$

$$=N\ln\left[\frac{(2\pi mkT)^{\frac{1}{2}}}{h}2\bar{A}_E\cdot 2\right]. \tag{43'}$$

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For a crystal,

$$S=k\left[\ln Q+T\frac{d\ln Q}{dT}\right],$$

so that for this crystal

$$S=R\left[\ln\left\{\frac{(2\pi mkT)^{\frac{1}{2}}}{h}2\bar{A}_E\right\}+\ln 2+1\right]. \quad (44)$$

Now $2\bar{A}_E$ is a "natural" cell size to take for the vibration of an atom in this crystal, since if the crystal were vibrating with all of its energy in its mode of highest frequency the motion of each atom would in fact be confined to such a cell. Moreover, such a cell can be assigned to each atom without any overlapping, and with none of the length of the crystal left unaccounted for. If this identification is made, (44) shows that the crystal has a communal entropy of $R\ln 2$. As compared with (34) it also has an extra entropy of $(1/2)R$ caused by the temperature variation of $\bar{A}_E$.

Rice[20] considers a different "natural" cell, corresponding to the vibration of the i'th atom when atoms $i+1$ and $i-1$ are held fixed. It is easy to show that, for this mode, $\nu_F=1/2\pi(2f/m)^{\frac{1}{2}}$ or

$$\bar{A}_F=(\pi kT/2\cdot 2f)^{\frac{1}{2}}=\frac{1}{\sqrt{2}}(\pi kT/2f)^{\frac{1}{2}} \quad (45)$$

this makes

$$\bar{A}_F=\sqrt{2}\bar{A}_E, \quad \text{or} \quad 2\bar{A}_E=\sqrt{2}\bar{A}_F. \quad (46)$$

It is, again, "natural," to assign a cell of length $\bar{A}_F$ to each atom, for if each one is given this length extending, say, in the direction of positive x, the whole length of the crystal can once more be thought of as accounted for without overlapping. Taking this interpretation, we get

$$S=R\left[\ln\left\{\frac{(2\pi mkT)^{\frac{1}{2}}}{h}\bar{A}_F\right\}+\ln(2\sqrt{2})+1\right], \quad (47)$$

in agreement with Rice. This would make the communal entropy $\frac{3}{2}R\ln 2$.

This example is instructive as illustrating the essentially arbitrary nature of the whole idea of cells and of communal entropy. The actual entropy of the crystal, from (43) is

$$S=R\left[\ln\left\{\frac{(2\pi mkT)^{\frac{1}{2}}}{h}\left(\frac{2\pi kT}{f}\right)^{\frac{1}{2}}\right\}+1\right], \quad (48)$$

and even here the argument of the logarithm has been taken apart into factors in a way which can be justified only on grounds of convenience. Such forms as (44) and (47) can have the same justification, but neither is unique. If we may say so, the crystal itself does not know that its atoms move in cells, nor what size the cells should be. Correspondingly, it does not know how much of its entropy is communal, and how much should be called by other names.

In fact, it is not necessary to use the idea of communal entropy in condensed phases at all if the cell sizes are chosen, as they could be, to account exactly for the whole entropy without leaving any residue. In gases also, the idea of communality of volume could be dispensed with, since the term R in the entropy need not be associated with the volume contribution; as shown above, it arises from $\ln N!$ and $N!$ is introduced to account for the indistinguishability of the molecules. We shall continue to use communal entropy as a working tool, however, since it gives us a way of making rather good estimates of thermodynamic entropies from physical considerations involving cell sizes. To complete our discussion of it we now proceed to show that it is possible to think of gases and condensed phases as being fundamentally the same in the communality which they display.

FLUCTUATION ENTROPY

In assigning a cell volume $2\bar{A}_E$ in the linear crystal we are asserting that while we know that an atom is in its cell, we do not know its position inside the cell. In assigning such a cell to each atom, we assert that after we have located one atom in its cell (purchasing this knowledge at the price of the term $k\ln(2\bar{A}_E)$ in the entropy) we still know nothing of the location within their cells of any of the other atoms. If only the one mode of vibration were excited, however, as in the pseudo-Einstein picture above, this would not be true, for in that mode the phases and amplitudes of all the ξ_i are related. From this point of view, then, the effect of the distribution of frequencies and wave-lengths is to destroy the correlation of phase between the motions of the

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TABLE I. The fluctuation factor α in monatomic crystals.

Substance	M	Θ	$T°K$	P_{mm}	$\Delta H_{cal./mole}$	$\log \alpha$	α
Argon	39.94	80[k]	77.48	200.6[b]	1880[a]	0.63	4.25
Krypton	83.7	63[k]	102.63	110.98[c]	2540[a]	0.89	7.76
Xenon	131.3	55[j]	143.2	132.2[d]	3850[a]	0.39	2.45
Magnesium	24.32	290[h]	734.8	2.27×10^{-2} [e]	35,300[a]	0.25	1.78
Zinc	65.38	235[i]	619.0	7.76×10^{-3} [e]	30,200[a]	0.77	5.89
Cadmium	112.41	168[i]	523.0	4.82×10^{-3} [f]	26,420[a]	0.72	5.25
Mercury	200.6	97[i]	223.1	4.5×10^{-7} [g]	15,210[a]	0.75	5.62

[a] K. K. Kelley, Bull. 383, U. S. Bureau of Mines, Washington, 1935.
[b] F. Born, Ann. d. Physik. **69**, 473 (1922).
[c] W. H. Keesom, J. Mazur, and J. J. Meihuizen, Physica **2**, 669 (1935).
[d] K. Peters and K. Weil, Zeits. f. physik. Chemie **A148**, 27 (1930).
[e] F. F. Coleman and A. Egerton, Phil. Trans. Roy. Soc. **A234**, 177 (1935).
[f] A. Egerton, J. Chem. Soc. **123**, 3024 (1923).
[g] A. Eucken, Landolt-Bornstein *Physikalisch-chemische Tabellen* fifth edition Supp. II b, p. 1292.
[h] F. Simon, Landolt-Bornstein *Physikalisch-chemische Tabellen* fifth edition Supp. II b, p. 1232.
[i] Fowler and Guggenheim, *Statistical Thermodynamics*, p. 145.
[j] K. Clusius and L. Riccoboni, Zeits. f. Physik. Chemie **B38**, 81 (1937).
[k] K. Clusius, Zeits. f. physik. chemie **31B**, 459 (1936).

atoms in this one mode. Another effect is to produce motions—surgings, swayings, or fluctuations—of the center of the cell, enabling whole sections of the crystal to encroach on each other. This produces communal entropy, i.e., entropy associated with the non-exclusiveness of the cells.[22] On the face of it this seems to be different in kind from the communal entropy in a gas, where the molecules are assigned such large cells that many molecules (for a perfect gas an infinite number of them) can be in one cell. A little reflection shows, however, that, whether in a gas, a liquid, or a crystal, the occasion for considering communal entropy arises only because of the occurrence of fluctuations in density, and that the communal entropy we have described for a crystal is really the same thing as is found in a gas.* We therefore propose the name *fluctuation entropy* as an alternative for the term communal entropy. Our earlier discussion of the entropy contribution due to temperature variability of cell-size shows that this is also a fluctuation entropy. Since in crystals the temperature variability of cell size and the encroachment of one atom upon another are not independent, we shall use the term fluctuation entropy to refer to the extra entropy from whatever "cause," which must be added to cell-volume entropies as calculated from models.

[22] Cf. O. K. Rice, J. Chem. Phys. **6**, 476 (1938).

* This is paradoxical from the point of view adopted in discussing (7). The paradox can be resolved by remembering that it is only "free volume" which is shared in condensed phases, and all of the free volume is accessible for sharing. In a gas (practically) the whole volume is free volume.

REAL CONDENSED SYSTEMS

Our program now calls for the application of the ideas developed in the foregoing sections to real systems. We shall find that the study of simple real systems (crystals) fills enough of the remaining gaps in the picture to provide a representation which can be used with some confidence for complicated real systems (liquids), with the purpose of deriving, or interpreting, relationships connecting entropy changes with other experimental quantities and with the known structural features of individual substances.

As a suitable starting point, we may consider the process of vaporization of a liquid or a solid. From (28′) the molal entropy change may be written

$$\Delta S = R \ln (V_{fg}/\gamma V_{fc}), \tag{49}$$

V_{fg} being molal free volume in the gas and V_{fc} that in the condensed phase. Subject to the conditions previously discussed, (49) is a general equation.

For practical purposes, and unless otherwise noted, we absorb into γ the difference (usually small in the cases of interest) between the actual entropy of the vapor (saturated or not) and that of the same substance reduced to a suitable standard state as a perfect gas, writing

$$\Delta S = R \ln (V_g/\gamma V_{fc}). \tag{50}$$

There are now several possible paths which might be followed. One, which exemplifies the way in which the method can be used, is to

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write, for an *equilibrium* vaporization,

$$\ln (V_g/\gamma V_{fc}) \simeq \Delta S/R = \Delta H/RT,$$
$$V_g/\gamma V_f = RT/P_g \gamma V_f = e^{\Delta H/RT}, \quad (51)$$
$$P_g = RT/\gamma V_f e^{-\Delta H/RT}.$$

MONATOMIC CRYSTALS

Equation (51) (without γ) for the vapor pressure of a condensed phase has been derived by various writers[3] by methods essentially equivalent to the one employed here. In principle, it may be applied in any case for which estimates of V_f and γ can be made. We shall use it, with data for the solid-vapor equilibrium for some monatomic solids, to complete our free volume picture.

As a first step in obtaining V_f for a monatomic crystal one can take (43′) for ln Q for the linear crystal, and multiply by 3 to get ln Q for a three-dimensional crystal in which the motions in the three directions are independent of each other. This gives

$$\ln Q = N\left[\ln\left\{\frac{(2\pi mkT)^{\frac{1}{2}}}{h^3}\right\} + \ln (2\bar{A})^3 + \ln 8\right]. \quad (52)$$

Here $N\cdot(2\bar{A})^3\cdot 8$ is a free volume. We have seen, however, that even in the linear case the interaction of the atomic motions introduces some arbitrariness in the magnitude of the fluctuation entropy to be added. The best we can hope to do here, therefore, is to write

$$2\bar{A}' = (\pi kT/2f')^{\frac{1}{2}} = \frac{1}{\nu}(kT/2\pi m)^{\frac{1}{2}} \quad (53)$$

for some frequency ν and substitute for the ln 8 in (52) a term ln α, using the disposable constant α to represent the fluctuation factor appropriate to the choice of ν which defines the cell size. α will also, as used here, be appropriate to the implied cubic cell shape. It is partly our ignorance of what effective shape a cell should have which requires the use of a disposable constant.

We can guess that, for a plausible choice of ν, α will be of order of magnitude unity. Remembering that V_f is made up of "full" cells and therefore should have an e in the denominator, in analogy with (7′), and that $(\bar{A}')^3$ is proportional to $T^{\frac{3}{2}}$, we may write

$$V_f = N\left[\frac{1}{\nu}(kT/2\pi m)^{\frac{1}{2}}\right]^3 \alpha e^{\frac{1}{2}}. \quad (54)$$

Since for a monatomic vapor, at low pressure, γ must be very nearly equal to 1, this converts (51) to

$$P = \frac{(2\pi m)^{\frac{3}{2}}\nu^3}{(kT)^{\frac{3}{2}}\alpha e^{\frac{1}{2}}} e^{-\Delta H/RT} \quad (55)$$

for the vapor pressure of the crystal, a form identical, except for the factor $\alpha e^{\frac{1}{2}}$, with one given in 1903 by Mie[23] for liquids.

For ν we may choose a Debye characteristic frequency calculated from heat capacity data (for some one temperature). The physical meaning of this choice cannot be stated precisely, since we do not know the true distribution of frequencies in the solid,[24] and, therefore, cannot tell just what kind of an average the Debye treatment represents. This sort of uncertainty is already provided for in α. We may also allow α to take up whatever uncertainty is introduced through the necessity of using for m an average over the masses of the various isotopic species which may be present.

Except for α, (55) is now a relation between experimental quantities, and there are a number of substances for which the necessary data exist for a calculation of α. In Table I appear the results of such a calculation for some crystalline elements which are volatile enough to permit the experimental measurement of vapor pressures. Writing $h\nu = k\Theta$, (55) gives

$$P = \frac{(2\pi)^{\frac{3}{2}}k^{5/2}}{N^{\frac{3}{2}}h^3 e^{\frac{1}{2}}} \cdot \frac{M^{\frac{3}{2}}\Theta^3}{T^{\frac{1}{2}}} \cdot \frac{1}{\alpha} \cdot e^{-\Delta H/RT} \quad (55')$$

where N = Avogadro's number and M is the conventional atomic weight. This gives

$$\log \alpha = \log\left[\frac{M^{\frac{3}{2}}\Theta^3}{PT^{\frac{1}{2}}}\right] - 0.4343\frac{\Delta H}{RT} + \log C,$$
$$\log C = \log\left\{\frac{(2\pi)^{\frac{3}{2}}k^{5/2}}{N^{\frac{3}{2}}h^3 e^{\frac{1}{2}}}\right\} \quad (56)$$

and takes the value 1.0723, if P is in millimeters of mercury.

[23] G. Mie, Ann. d. Physik 11, 657 (1903).
[24] E.g., M. Blackman, Proc. Roy. Soc. London **A159**, 416 (1931); E. W. Montroll, J. Chem. Phys. 11, 481 (1943).

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It is observed that the values of α cluster around 5. This corresponds to fluctuations in position of the unit cells which have the effect of making each linear dimension greater by a factor of $5^{\frac{1}{3}}=1.71$ than it would be if the cells were stationary. The exact numerical values of α cannot be interpreted nor compared without more discussion than we propose to give here. We may point out, however, that (55′), with the thermodynamic requirement $d\ln P/dT=\Delta H/RT^2$, contains a relation between the temperature variations of α, Θ, and ΔH. Although we have computed α at random temperatures, it is of interest to consider the orders of magnitude of the various quantities in the picture. These can be seen by calculating

$$2\bar{A}'=\frac{T}{\Theta}\cdot\frac{hN}{(2\pi MRT)^{\frac{1}{2}}}=\frac{1.59\times10^{-3}}{(MRT)^{\frac{1}{2}}}\cdot\frac{T}{\Theta}.$$

For argon, at the temperature used above, $2\bar{A}'=3.04\times10^{-9}$ cm. In solid argon, the distance apart of two alternate atoms[25] (which form the "boundaries" of the box containing the one between them) is 7.68A. This means that the "free length" for an atom is $0.304/7.68\times100=4.0$ percent of the internuclear distance of its "wall" neighbors. Multiplication by $\alpha^{\frac{1}{3}}$ gives 4.93×10^{-9} cm or 6.47 percent of the wall-to-wall distances. $V_f=\alpha e^{\frac{1}{3}}(2\bar{A}')^3\times6\times10^{23}=0.118$ cc. Since the molal volume of the solid is about 22.4 cc, $V_f/V_s=0.00525$. For cadmium at the temperature used $2\bar{A}'=2.24\times10^{-9}$ cm or 3.8 percent of one of the wall-to-wall distances. With fluctuations (multiplied by $\alpha^{\frac{1}{3}}$) this becomes 6.6 percent. $V_f=.0588$ cc and $V_f/V_s=0.00453$.

These numbers all seem reasonable, and support the idea that some real significance attaches to the picture we have developed of the free volume in a solid.

An approach to the solid state which is more reminiscent of the conventional one can be made by substituting (53) into (52), and using

$$h\nu=k\Theta \quad \text{and} \quad S=R\left[\ln Q+T\frac{d\ln Q}{dT}\right].$$

This gives

$$S_c=R\left[\ln\left(\frac{T}{\Theta}\right)^3+\ln\alpha+3\right], \qquad (57)$$

where α has the same meaning as before. (57) becomes equal to the high temperature limit for S for the Einstein solid if $\alpha=1$, and for the Debye solid if $\alpha=e$.[26]

A fuller discussion of this and other points involved in a free volume treatment of solids must be left for a separate paper. We may recall here, however, that α as we have evaluated it depends on the way in which we chose to define the cell volume available to an atom. Our choice corresponded to (44) for the one-dimensional case. If we had taken Rice's choice (Cf. (46) (47)) the cell would have been smaller, and α larger, by a factor of $2^{\frac{3}{2}}=2.828$, giving values in the neighborhood of 14. This is still smaller than the communality factor $e^3=20.0855$ proposed by Rice[22] for a solid of hard elastic spheres. It will be observed, however, that we have adopted the physical idea of communality in solids which, so far as the writer is aware, Rice was the first to propose.[20] His qualitative idea that, with "natural" choices of cell volumes in both cases, fluctuation entropies in solids will, in general, be larger than those in gases (where $\alpha=1$, by our conventions) is also confirmed by the numerical results we have obtained. In the following paper it will be found that liquids (again, for a "natural" definition of cell volume) fall between solids and gases in this respect.

[25] *International Critical Tables*, Vol. I, p. 340.

[26] Cf. J. E. Mayer and M. G. Mayer, footnote 1, p. 322.

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