The integral is evaluated by partial functions or contour integration. The result, which is independent of r and ρ, agrees with (5).

The power spectrum of b_s can be obtained similarly. In fact, one gets for this just the right-hand side of (11) with r and ρ interchanged and l and c interchanged. Consequently

$$\langle b_s^2\rangle_{\text{Av}}=2kT/Ll \tag{13}$$

again in agreement with (5).

For a line with open ends the coordinates a_s and b_s will be defined by

$$V=\sum a_s\cos(\pi sy/L),\quad I=\sum b_s\sin(\pi sy/L). \tag{14}$$

One finds that the power spectra and consequently the mean square values of a_s and b_s are again given by the expressions obtained above.

IV. LONG TRANSMISSION LINE

A very long transmission line with arbitrary terminal conditions can be treated as follows. The actual normal coordinates for the undamped system will depend on the capacities and inductances of the terminal impedances. Suppose that, in spite of this, one introduces coordinates defined by (3). Then, although the Eq. (7) is no longer imposed by the boundary conditions, the relation (8) will hold for all points P such that a disturbance of any frequency originating at P does not extend to the end of the line. Thus for a sufficiently long line, one may suppose (8) to hold at all points, the contribution of the end portions to the final integrals being a negligible fraction of the whole. The results (11), (12), and (13) will therefore still hold.

The same conclusion would follow if coordinates defined by (14) were introduced. Consequently, for a long line terminated in an arbitrary way, the equipartition results hold in their simple form.

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Statistical Mechanics of Mixtures of Isotopes*

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The excess free energy of a mixture of isotopes is expanded in a Taylor series in powers of the relative mass differences $(m_0-m_j)/m_j$, where m_j and m_0 are the masses of the particles of the jth component and of a reference isotope, respectively. This expansion is only useful if it assumed that all the particles in the mixture obey classical or Boltzmann statistics. When this assumption is made it is found that the linear term in the expansion vanishes identically. The second-order term has the form $\Sigma_i{}^s\Sigma_j{}^s x_ix_j(\lambda_i-\lambda_j)^2\cdot Q$, where Q is a universal function of m_0, T, and V, λ_j equals $(m_0-m_j)/m_j$, and x_j is the mole fraction of the jth component. This expression gives the explicit dependence of the excess free energy on the mole fractions and on the relative mass differences λ_j. From this result it can be shown, among other things, that a phase separation of the isotopes in a mixture should take place at a sufficiently low temperature. It can also be shown that there is an approximate law of corresponding states between different mixtures of isotopes. The theory is directly applicable to all solid mixtures and to fluid mixtures of the hydrogen isotopes. Unfortunately owing to the lack of experimental data it is impossible to test the theory rigorously. Finally it is shown how the theory can be used to interpret the behavior of He^3-He^4 solutions. When sufficient experimental data becomes available the theory should throw considerable light on the influence of quantum statistics on the properties of these solutions.

1. INTRODUCTION

THE purpose of this paper is to develop an approximate theory of mixtures of isotopes. It is of course well known[1] that if the atoms or molecules of a mixture of isotopes are assumed to obey the laws of classical mechanics then the thermodynamic properties of the mixture can easily be related to those of the pure isotopes. Such mixtures are in fact "ideal solutions." However, if we assume that the particles of the system obey the laws of quantum mechanics then it is impossible to express, in any general way, the properties of a mixture of isotopes in terms of those of its components. Now we know, that, except at very low temperatures, the physical properties of most substances can be accurately accounted for by means of classical statistical mechanics. Consequently the properties of solutions of isotopes will remain ideal until these temperatures are reached. If we limit our attention to the class of simple substances to which De Boer's quantum mechanical law of corresponding states[2] applies, then we can easily estimate the highest temperature at which any particular mixture can be expected to show deviations from ideal behavior. For example, we find that (gaseous) mixtures of helium and hydrogen isotopes are unlikely to show nonideal behavior above 30°K and 60°K, respectively. These two substances are, however, the only ones that show appreciable departures from classical behavior in the gaseous and liquid states; all

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* Contribution number 1301 from the Sterling Chemistry Laboratory.

[1] E. A. Guggenheim, *Mixtures* (Cambridge University Press, Cambridge, 1952), Chap. 2.

[2] J. De Boer, Physica 14, 139 (1948).

other substances solidify before any departures from classical behavior appear. We can therefore conclude that, apart from these substances, mixtures of isotopes will be ideal in the liquid and gaseous states.

The theory we shall develop is based on the following three assumptions.

(a) We shall assume that the atoms or molecules of the system (for simplicity we shall henceforth refer to these as "particles") are "rigid." That is to say we assume that the motions of the electrons and nuclei, relative to the mass center of one of the particles, are not influenced by the presence of the other particles in the system. If we make this assumption then the partition function of the system immediately factorizes into two factors, Z_1 and Z_2. Here Z_1 is the partition function for the motions of the electrons and nuclei relative to the mass centers of the particles and Z_2 is the partition function for the motions of the mass centers themselves. Now the variation in Z_1 due to the difference between the masses of the isotopes makes no contribution to the free energy of mixing.[1] We can therefore ignore Z_1 and concentrate our attention entirely on Z_2, which we shall write simply as Z.

(b) Next we shall assume that the particles of all the isotopes in the mixture obey classical or Boltzmann statistics. While this assumption is not generally justified there are two important cases in which it is likely that it can be regarded as an accurate approximation. First, we should expect it to be a good approximation for the hydrogen isotopes. This is because the different types of statistics obeyed by the molecules of these isotopes arise from their different spin states. Consequently if the different spin states of the molecules exert a marked influence on the properties of the isotopes then we should expect a considerable difference in the properties of the *ortho* and *para* species of any particular isotope. The properties of the two species are, however, very nearly identical; they amount at the most to about 1%. We can therefore assume that the properties of the hydrogen isotopes are very nearly independent of the spin states of their molecules; consequently we can assume that they obey Boltzmann statistics. The accuracy of this assumption can very easily be tested by comparing the properties of mixtures of hydrogen isotopes that have different *ortho-para* concentrations. If the properties of the mixtures depend strongly on the *ortho-para* concentrations of the various concentrations of the various components then we must conclude that our assumption is unjustified. Secondly we should expect the assumption to be an accurate approximation for mixtures of isotopes in the solid state. For, in the solid state the particles in the system can usually be regarded as being localized on lattice sites, and it is well known[3] that in such a system both Fermi-Dirac and Bose-Einstein statistics reduce to Boltzmann statistics.

On the other hand, this assumption is unlikely to be an accurate approximation for liquid or gaseous mixtures of He^3 and He^4. This is because the properties of these substances appear to depend critically on the type of statistics obeyed by their atoms. However, we shall see in Sec. 4 that if we use the theory in an indirect manner we can throw considerable light on the behavior of these solutions.

(c) Finally we assume that the interaction potential between the particles of any isotope is independent of the mass of the isotope. This assumption, while very accurate, is not completely correct for the following reason. The interaction potential depends on the electron density distribution round the nuclei. Now the reduced electron masses enter into this distribution and these in turn depend on the mass of the nuclei. However if the mass of the nuclei is changed by an amount δM then the reduced electron masses will change by an amount of the order of $10^{-3}\,\delta M$. This change is so small that it can be neglected entirely and consequently the interaction potential between the particles can be considered to be independent of the mass of the nuclei.

In the next section we give the formal mathematical development of the theory. This is based on the perturbation expansion of the partition function Z.[4,5] The expansion parameters are the relative mass differences $(m_0-m_j)/m_j$, where m_j is the mass of the jth component and m_0 is the mass of the particles of a reference isotope. The way in which these parameters enter into the partition function can readily be seen from the Hamiltonian of the system. Suppose we have a mixture of s isotopes. Let m_i and $x_i=N_i/N$ be the mass and the mole fraction of the ith component. Then we can write the total Hamiltonian, H, for the mixture in the form,

$$H=-\sum_{i=1}^{s}(1/m_i)\sum_{j=1}^{N_i}(\hbar^2/2)\nabla_{r_j}{}^2+V(\mathbf{r}_1\cdots\mathbf{r}_N),\tag{1.1}$$

where $\mathbf{r}_1\cdots\mathbf{r}_N$ are the coordinates of the N particles and $V(\mathbf{r}_1\cdots\mathbf{r}_N)$ is the total interaction potential of all the particles. From assumption (c) this potential is independent of the masses m_j. To simplify the notation we write $k_j=(-\hbar^2/2)\nabla_{r_j}{}^2$ and set

$$K(N_i,m_i)=(1/m_i)\sum_{j}^{N_i}k_j.$$

With this notation the Hamiltonian becomes

$$H=\sum_{i=1}^{s}K(N_i,m_i)+V(\mathbf{r}_1\cdots\mathbf{r}_N).\tag{1.2}$$

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[3] R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, Cambridge, 1936), Chap. 2.

[4] M. R. Schafroth, Helv. Phys. Acta **24**, 645 (1951).

[5] G. V. Chester, Phys. Rev. **93**, 606 (1954). The author wishes to thank Dr. Schafroth for pointing out to him that many of the results obtained in this paper had been found earlier by Dr. Schafroth in the paper quoted above.

Now,

$$K(N_i,m_i)=\frac{1}{m_i}\sum_{j=1}^{N_i} k_j$$

$$=\frac{1}{m_0}\sum_{j=1}^{N_i} k_j+\frac{m_0-m_i}{m_i}\cdot\frac{1}{m_0}\sum_{j=1}^{N_i} k_j, \tag{1.3}$$

and if we set $\lambda_i=(m_0-m_i)/m_i$ we have,

$$K(N_i,m_i)=K(N_i,m_0)+\lambda_i K(N_i,m_0).$$

The Hamiltonian can therefore be written in the form,

$$H=\sum_{i=1}^{s} K(N_i,m_0)+V+\sum_{i=1}^{s}\lambda_i K(N_i,m_0), \tag{1.4}$$

that is,

$$H=K(N,m_0)+V+\sum_{i=1}^{s}\lambda_i K(N_i,m_0). \tag{1.5}$$

Finally, if we define H_0 by the equation

$$H_0=K(N,m_0)+V, \tag{1.6}$$

then H becomes

$$H=H_0+\sum_{i=1}^{s}\lambda_i K(N_i,m_0). \tag{1.7}$$

The free energy to the system can therefore be considered as a function of the λ_i's and we can formally expand it as a Taylor series in these parameters. Clearly we may expect such a series to be physically useful as long as the λ_i are not too large. We can also express the Hamiltonian for N particles of one of the pure isotopes in a similar way. Thus,

$$H_i=H(N,m_i)=H_0+\lambda_i K(N,m_0), \tag{1.8}$$

and we can again expand the free energy in powers of λ_i. Our method is therefore as follows. We expand the free energy of the mixture in powers of the λ_i's and we also expand the free energy of each of the pure isotopes in a similar series. From these series we can at once obtain a formal expansion of the free energy of mixing in powers of the λ_i's. The first term in this expansion gives the ideal free energy of mixing. The term that is linear in the λ_i vanishes identically and we have to include terms that are quadratic in the λ_i in order to obtain any departures from ideal behavior. This term is calculated explicitly as a function of the x_i and λ_i. An important feature of this method is that no assumption is made about the state of aggregation of the mixture and the theory should therefore be equally applicable to solid, liquid and gaseous mixtures. In Sec. 3, we discuss the physical consequences of the expression we have obtained for the excess free energy of mixing. The principal results that emerge from this discussion are: (a) that mixtures of isotopes should exhibit very nearly ideal behavior, this conclusion follows directly from the fact that the excess free energy depends only on second and higher powers of the relative mass differences, (b) that the free energy of mixing has the same dependence on the mole fractions as that of a "regular" solution,[6] (c) that at sufficiently low temperatures the excess free energy of mixing is always positive, consequently we expect a phase separation of the isotopes to take place at some temperature above absolute zero, and (d) that there exists an approximate law of corresponding states between mixtures of different isotopes. Unfortunately, we have not been able to express the excess free energy in terms of the properties of pure isotopes. The best we have been able to do is to obtain an upper bound for the excess free energy in terms of measurable quantities. There appears to be very little experimental data with which to compare the theory. In fact, only a qualitative comparison can be made; this comparison is however satisfactory. We conclude this section by discussing the experimental data that are required to test the theory rigorously.

In Sec. 4, we turn to a discussion of $\mathrm{He}^3-\mathrm{He}^4$ solutions. Our aim here is to throw some light on the influence of quantum statistics on the properties of these solutions. Now the theory we have developed is only valid if the particles of all the isotopes in the mixture obey Boltzmann statistics. Therefore if we compare the predictions of our theory with the experimental properties of $\mathrm{He}^3-\mathrm{He}^4$ solutions we should be able to show how the properties of these solutions are influenced by the different types of quantum statistics obeyed by He^3 and He^4 atoms. Thus if the experimental properties are in good agreement with the predictions of the theory then we can conclude that the properties of the solutions are not appreciably influenced by the different types of statistics obeyed by the atoms. On the other hand if there are large discrepancies between the predictions and the experimental data then we must draw the opposite conclusion. What little data are available indicates that at about 3°K the predictions and experimental data are in qualitative agreement but that at lower temperatures there are large discrepancies.

The only other work on the theory of isotopes appears to be that due to Prigogine.[7–9] Although his method of approach is very different from ours he has obtained very similar physical results. In Sec. 5 we shall compare these with our own.

2. FREE ENERGY OF MIXING

We consider a mixture of s components each of which is an isotope of the same substance. If m_i and x_i $(=N_i/N)$ are the mass and the mole fraction of the ith component then we have seen that the Hamiltonian of this system can be written in the form,

$$H=H_0(N,m_0)+\sum_{i=1}^{s}\lambda_i K_i, \tag{2.1}$$

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[6] E. A. Guggenheim, reference 1, Chap. 4.

[7] Prigogine, Bingen, and Jeener, Physica **20**, 383 (1954).

[8] I. Prigogine and J. Jeener, Physica **20**, 516 (1954).

[9] Prigogine, Bingen, and Bellemans, Physica **20**, 633 (1954).

where for convenience we have set $K_i = K(N_i, m_0)$. Likewise the Hamiltonian of the ith component can be written,

$$H_i = H_0(N, m_0) + \lambda_i K. \tag{2.2}$$

Now the free energy of the mixture, which we denote by $F_m(N_1 \cdots N_s, m_0, \lambda_1 \cdots \lambda_s)$ is given by

$$F_m(N_1 \cdots N_s, m_0, \lambda_1 \cdots \lambda_s) = -kT \log Z, \tag{2.3}$$

where

$$Z = \mathrm{Tr}[\exp(-\beta H)]. \tag{2.4}$$

In this last equation $\beta = 1/kT$, T is the absolute temperature, k is Boltzmann's constant, and the symbol $\mathrm{Tr}(A)$ stands for the trace of the operator A. Since we have assumed that all the different types of particles in the mixture obey Boltzmann statistics all the traces that occur in the theory must be formed with unsymmetrized wave functions. We now formally expand F_m in a Taylor series in the parameters λ_i. Thus,

$$F_m = F_m(N_1 \cdots N_s, m_0, 0) + \sum_{i=1}^{s} \lambda_i [\partial F_m / \partial \lambda_i]_{\lambda=0}$$
$$+ \tfrac{1}{2} \sum_{i=1}^{s} \sum_{j=1}^{s} \lambda_i \lambda_j [\partial^2 F_m / \partial \lambda_i \partial \lambda_j]_{\lambda=0} + O(\lambda^3), \tag{2.5}$$

where λ stands for the set $\lambda_1 \cdots \lambda_s$. We now calculate the derivatives of F_m in terms of those of Z. Using Eq. (2.3) we find that

$$[\partial F_m / \partial \lambda_i]_{\lambda=0} = -[kT / Z(m_0, 0)][\partial Z / \partial \lambda_i]_{\lambda=0}, \tag{2.6}$$

and

$$[\partial^2 F_m / \partial \lambda_i \partial \lambda_j]_{\lambda=0} = (kT/Z^2)[\partial Z/\partial \lambda_i \cdot \partial Z / \partial \lambda_j]_{\lambda=0}$$
$$- (kT/Z)[\partial^2 Z / \partial \lambda_i \partial \lambda_j]_{\lambda=0}. \tag{2.7}$$

We next calculate the derivatives of Z with respect to the λ_i by means of the perturbation expansions for the partition function[5]; we find that,

$$[\partial Z / \partial \lambda_j]_{\lambda=0} = -\beta \textstyle\sum_l (K_j)_{ll} \exp(-\beta E_l), \tag{2.8}$$

and

$$[\partial^2 Z / \partial \lambda_i \partial \lambda_j]_{\lambda=0} = \beta^2 \sum_{l_1} \sum_{l_2} (K_i)_{l_1 l_2} (K_j)_{l_2 l_1} G_{l_1 l_2}, \tag{2.9}$$

where $G_{l_1 l_2}$ is given by,

$$G_{l_1 l_2} = [\exp(-\beta E_{l_1}) - \exp(-\beta E_{l_2})] / \beta (E_{l_2} - E_{l_1}). \tag{2.10}$$

In these equations, the E_{l_i} are the energy eigenvalues of the reference system of N particles of mass m_0 and the matrix elements $(K_i)_{l_1 l_2}$ are formed with the corresponding wave functions. It is now convenient to define the following two averaging operations,

$$\langle A \rangle = \textstyle\sum_l (A)_{ll} \exp(-\beta E_l) / \sum_l \exp(-\beta E_l), \tag{2.11}$$

and

$$\langle A, B \rangle = \sum_{l_1} \sum_{l_2} (A)_{l_1 l_2} (B)_{l_2 l_1} G_{l_1 l_2} / \sum_{l} \exp(-\beta E_l). \tag{2.12}$$

The matrix elements $(K_j)_{l_1 l_2}$ in Eqs. (2.8) and (2.9) are given by equations of the form,

$$(K_j)_{l_1 l_2} = \sum_{t=1}^{N_j} (k_t)_{l_1 l_2}, \tag{2.13}$$

where we have absorbed the factor $(m_0)^{-1}$ into k_t. If we combine Eqs. (2.11), (2.12), and (2.13) with Eqs. (2.8) and (2.9) we find that

$$\left[\frac{1}{Z} \frac{\partial Z}{\partial \lambda_i}\right]_{\lambda=0} = -\beta \langle K_i \rangle = -\beta \sum_{t=1}^{N_i} \langle k_t \rangle, \tag{2.14}$$

and

$$\left[\frac{1}{Z} \frac{\partial^2 Z}{\partial \lambda_i \partial \lambda_j}\right]_{\lambda=0} = \beta^2 \langle K_i, K_j \rangle = \beta^2 \sum_{r=1}^{N_i} \sum_{t=1}^{N_j} \langle k_r, k_t \rangle. \tag{2.15}$$

Now $\langle k_i \rangle$ is the average value of the kinetic energy of the ith particle, averaged over all accessible states of the reference system. It is therefore independent of the suffix i; to indicate this we set $\langle k_i \rangle = \langle k_\alpha \rangle$, where α refers to any particle of the reference system. Similarily $\langle k_r, k_t \rangle$; $r \neq t$ is independent of the pair of particles that we chose and we can set it equal to $\langle k_\alpha, k_\beta \rangle$; $\alpha \neq \beta$. The suffixes r and t can, however, be equal and in this case we have to set $\langle k_r, k_r \rangle$ equal to $\langle k_\alpha, k_\alpha \rangle$. Using this notation we can write Eqs. (2.14) and (2.15) in the following way,

$$(1/Z \partial Z / \partial \lambda_i)_{\lambda=0} = -\beta N_i \langle k_\alpha \rangle, \tag{2.16}$$

and

$$(1/Z \partial Z / \partial \lambda_i \partial \lambda_j)_{\lambda=0} = \beta^2 [N_i N_j \langle k_\alpha, k_\beta \rangle + \delta_{ij} N_i \Delta], \tag{2.17}$$

where Δ is given by,

$$\Delta = \langle k_\alpha, k_\alpha \rangle - \langle k_\alpha, k_\beta \rangle. \tag{2.18}$$

Substituting Eqs. (2.16) and (2.17) into Eqs. (2.6) and (2.7) we get,

$$(\partial F_m / \partial \lambda_i)_{\lambda=0} = N_i \langle k_\alpha \rangle = x_i \langle K \rangle, \tag{2.19}$$

and

$$(\partial^2 F_m / \partial \lambda_i \partial \lambda_j)_{\lambda=0}$$
$$= \beta [N_i N_j \langle k_\alpha \rangle^2 - N_i N_j \langle k_\alpha, k_\beta \rangle - \delta_{ij} N_i \Delta]$$
$$= \beta [x_i x_j \langle K \rangle^2 - x_i x_j (\langle K, K \rangle - N\Delta) - \delta_{ij} x_i N \Delta]. \tag{2.20}$$

These last two equations lead to the following expansion for the free energy of the mixture

$$F_m(N_1 \cdots N_s, m_0, \lambda_1 \cdots \lambda_s)$$
$$= F_m(N_1 \cdots N_s, m_0, 0) + \left(\sum_{i=1}^{s} x_i \lambda_i\right) \langle K \rangle$$
$$+ (\beta/2) \left(\sum_{i=1}^{s} \sum_{j=1}^{s} \lambda_i \lambda_j x_i x_j\right) [\langle K \rangle^2 - (\langle K, K \rangle - N\Delta)]$$
$$- (\beta/2) \left(\sum_{i=1}^{s} \lambda_i^2 x_i\right) N \Delta + O(\lambda^3). \tag{2.21}$$

Using exactly the same methods we can expand the free energy, F_i, of one mole of a pure isotope of mass m_i, thus,

$$F_i(N,m_0,\lambda_i)=F_i(N,m_0,0)+\lambda_i\langle K\rangle+(\beta/2)\lambda_i^2 \times[\langle K\rangle^2-(\langle K,K\rangle-N\Delta)]-(\beta/2)\lambda_i^2N\Delta. \quad (2.22)$$

We now have to examine the function

$$F_m(N_1\cdots N_s,m_0,0).$$

It is given by the equation,

$$F_m(N_1\cdots N_s,m_0,0)=-kT\log Z(N_1\cdots N_s,m_0,0),$$

where

$$Z(N_1\cdots N_s,m_0,0)=[\prod_j^s(N_j)!]^{-1}\sum_l \exp(-\beta E_l).$$

The factor

$$[\prod_{j=1}^s(N_j)!]^{-1}$$

in the last equation arises because the particles of the different isotopes in the mixture were originally distinguishable by their different masses. We can therefore write

$$Z(N_1\cdots N_s,m_0,0) =[N!/\textstyle\prod_j(N_j)!](N!)^{-1}\sum_l \exp(-\beta E_l),$$

and consequently,

$$F_m(N_1\cdots N_s,m_0,0) =F(N,m_0,0)+NkT\sum_{i=1}^s x_i\log x_i. \quad (2.23)$$

The excess free energy of mixing ΔF^E, is defined by the equation,

$$\Delta F^E=F_m-\sum_{i=1}^s x_iF_i-NkT\sum_{i=1}^s x_i\log x_i. \quad (2.24)$$

Therefore from Eqs. (2.21), (2.22), and (2.23) we find that,

$$\Delta F^E=(\beta/2)(\sum_{i=1}^s\sum_{j=1}^s x_ix_j\lambda_i\lambda_j-\sum_{i=1}^s x_i\lambda_i^2) \times[\langle K\rangle^2-(\langle K,K\rangle-N\Delta)]+O(\lambda^3). \quad (2.25)$$

This equation gives the explicit dependence of ΔF^E on the x_i and λ_i. It is clear from the method of derivation that it would be a simple, though tedious, matter to calculate as many terms in the expansion as we wish.

The first factor on the right of Eq. (2.25) is easily shown to be equal to

$$-\sum_{i<j}^s\sum x_ix_j(\lambda_i-\lambda_j)^2,$$

and is therefore negative for all values of the x_i and λ_j. We now shorten the notation by writing

$$\Delta F^E=c(x,\lambda)Q(T,V,m_0), \quad (2.26)$$

where x and λ stand for the sets (x_i) and (λ_i) respectively, and $c(x,\lambda)$, $Q(T,V,m_0)$ are given by

$$c(x,\lambda)=\sum_{i<j}^s\sum x_ix_j(\lambda_i-\lambda_j)^2, \quad (2.27)$$

and

$$Q(T,V,m_0)=(2kT)^{-1}[\langle K,K\rangle-\langle K\rangle^2-N\Delta]. \quad (2.28)$$

The function $Q(T,V,m_0)$ is a universal function of T,V and m_0; that is, it does not depend on either the x_i or λ_i. Unfortunately, we have not been able to express it in terms of the properties of the pure isotopes. However the following equation can easily be derived:

$$\langle K,K\rangle-\langle K\rangle^2=-kT[\partial^2F_i/\partial\lambda_i^2]_{\lambda_i=0}. \quad (2.29)$$

Now, since we can also show that $\langle K,K\rangle-\langle K\rangle^2$ and Δ are always positive, we find that ΔF^E must obey the following inequality:

$$\Delta F^E\leq-\tfrac{1}{2}[\partial^2F_i/\partial\lambda_i^2]_{\lambda_i=0}. \quad (2.30)$$

This equation provides us with an upper bound for ΔF^E; in the next section we shall show how we can determine $[\partial^2F_i/\partial\lambda_i^2]_{\lambda_i=0}$, approximately, from experiment.

Finally, it is easily shown that the "fluctuation" term Δ tends to zero as $T\rightarrow 0$. The sum of the other two terms in Q approaches $\sum_{l>0}|K_{l0}|^2/(E_l-E_0)$, as $T\rightarrow 0$, and the excess free energy is therefore positive at absolute zero. This completes the formal part of our work.

3. PHYSICAL CONSEQUENCES OF THE THEORY

In this section we shall first discuss the physical consequences of the formulas we have derived and afterwards we shall compare the predictions of the theory with experiment.

The fundamental formula for ΔF^E is

$$\Delta F^E=c(x,\lambda)Q(T,V,m_0), \quad (3.1a)$$

where

$$c(x,\lambda)=\sum_{i<j}^s\sum x_ix_j(\lambda_i-\lambda_j)^2, \quad (3.1b)$$

and

$$Q(T,V,m_0)=\tfrac{1}{2}\beta[\langle K,K\rangle-\langle K\rangle^2-N\Delta]. \quad (3.1c)$$

From these equations we can draw the following conclusions.

(a) The foregoing formulas were derived without making any assumptions about the state of aggregation of the system; they therefore apply quite generally to gaseous, liquid and solid mixtures.

(b) Equation (2.27) shows that ΔF^E depends only on second and higher order terms in the mass differences

λ_i. This makes it seem likely that mixtures of isotopes that obey Boltzmann statistics will, in general, show only very small deviations from ideal behavior. We shall see that this conjecture is confirmed by what little experimental data is available.

(c) We have seen that the excess free energy of mixing is positive at absolute zero. On the other hand the ideal free energy of mixing goes to zero as $T \to 0$. Therefore at some temperature above absolute zero we should expect a phase separation of the isotopes in the mixture. The highest temperature, T_c, at which this separation can occur is found, by the usual methods,[6] to be given by the conditions,

$$RT_c = \tfrac{1}{2}(\lambda_1 - \lambda_2)^2 Q(T_c, V, m_0), \quad x_1 = x_2 = \tfrac{1}{2}, \qquad (3.2)$$

where we have specialized to a binary mixture. Equation (3.2) must be regarded as a transcendental equation for T_c; clearly as long as Q is negative it has no solution. It is interesting to note that this phase separation is a purely quantum mechanical phenomenon. If the particles of the mixture were assumed to obey the laws of classical mechanics then the solution would always be ideal.

(d) Next we notice that Eq. (3.1) give the explicit dependence of ΔF^E on the mole fractions x_i. It is clear from this equation that if we know ΔF^E for any one set of concentrations x then we can at once predict it for any other set x'. For we have at once that

$$\Delta F^E(T,V,x') = [c(x',\lambda)/c(x,\lambda)]\Delta F^E(T,V,x). \qquad (3.3)$$

(e) Equation (3.1) also gives the explicit dependence of ΔF^E on the relative mass differences λ_i. Therefore if we have determined ΔF^E experimentally for one solution with mass differences λ and mole fractions x we can at once predict ΔF^E for any other solution with mass differences λ' and mole fractions x'. We have in fact,

$$\Delta F^E(T,V,x',\lambda') = [c(x',\lambda')/c(x,\lambda)]\Delta F^E(T,V,x,\lambda). \qquad (3.4)$$

This last equation really expresses a law of corresponding states for mixtures of isotopes. In fact Eq. (3.2) tells us that if we know ΔF^E for a solution and divide it by the appropriate value of $c(x,\lambda)$ then we obtain a universal function of T, V, and m_0. Clearly since these remarks apply to any other thermodynamic property of the solution we are justified in speaking of a law of corresponding states.

(f) We can easily show that $\Delta F^E \to 0$ as $T \to \infty$, or as $k \to 0$. Therefore we should expect ΔF^E to increase as the temperature of the mixture is lowered. However, it appears that the properties of pure isotopes become very nearly identical when we pass from the liquid to the solid phase. This is strikingly shown by the plots of the specific heats of the hydrogen isotopes that appear in the article by Wooley, Scott, and Brickwedde.[10] It seems likely therefore that ΔF^E will decrease sharply as the mixture solidifies.

(g) Equation (3.16) shows that ΔF^E has the same dependence on the mole fractions x_i as a "regular" solution. Our formula differs from that for a regular solution in that Q is function both of T and V (or P).

(h) Finally we note that Eq. (2.30) provides an upper bound for ΔF^E. To our degree of approximation we find that $[\partial^2 F_i/\partial\lambda_i^2]_{\lambda_i=0}$ is given by the equation,

$$\left[\frac{\partial^2 F_i}{\partial \lambda_i^2}\right]_{\lambda_i=0} = \frac{1}{\lambda_i\lambda_j(\lambda_i-\lambda_j)}[\lambda_i F_j - \lambda_j F_i - (\lambda_i - \lambda_j)F_0], \qquad (3.5)$$

where F_j is the free energy of a pure isotope of mass m_j. In principle therefore we can determine the upper bound for ΔF^E provided we know the free energies of two pure isotopes together with that of the reference species.

The only published data on mixtures of isotopes other than helium is that due to Kerr[11] and Hoge and Arnold.[12] Kerr measured the excess molar volume of a mixture of T_2, DT, and D_2 and found that it was about 0.6% of the total volume of the mixture. Unfortunately he worked with only one solution at fixed composition and we therefore cannot test either the dependence on the mole fractions or the approximate law of corresponding states predicted by the theory. However, the fact that the excess molar volume is so small is in good agreement with our prediction that isotopic solutions should be very nearly ideal. Hoge and Arnold measured the dew points pressures for two H_2-D_2 mixtures and for three H_2-HD mixtures. From their data, we can calculate the excess free energy of mixing for the solutions. The results of these calculations are tabulated in Table I. First we note that the values of ΔG^E range from 2% to 4% of the ideal free energies of mixing and are therefore comparitively small—as we have predicted. Let us take HD as the reference isotope. Then we find that $\lambda_1 = -\frac{1}{2}$ and $\lambda_2 = \frac{1}{4}$, for H_2 and D_2, respectively. Now solutions 3 and 5 both refer to the same temperature and roughly the same pressure. Consequently, from Eq. (3.1), we find that

$$\Delta G^E(3)/\Delta G^E(5) = (x_1x_2)_3/(x_1x_2)_5 \simeq 1.2,$$

which is in satisfactory agreement with experiment. Likewise solutions 1 and 3 refer to roughly the same temperature and pressure and we find that we should have,

$$\Delta G^E(3)/\Delta G^E(1) = \lambda_1^2(x_1x_2)_3/(\lambda_1-\lambda_2)^2(x_1x_2)_1 \simeq 0.5.$$

Again the agreement with experiment is satisfactory. Unfortunately this is as far as we can go with this type of comparison.

It is fairly clear from our discussion that the two

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[10] Wooley, Scott, and Brickwedde, J. Research Natl. Bur. Standards **41**, 379 (1948).

[11] E. C. Kerr, J. Am. Chem. Soc. **74**, 824 (1952).

[12] H. J. Hoge and R. D. Arnold, J. Research Natl. Bur. Standards **47**, 63 (1951).

TABLE I. Excess free energy of mixing for solutions investigated by Hoge and Arnold (reference 12).

Solution No.	1	2	3	4	5
Temperature (T) °K	19.00	20.00	18.00	17.03	18.00
Pressure (P) mm/Hg	234±2	322±2	280±1	158±1	286±1
Mole fraction H_2	0.499	0.460	0.503	0.503	0.752
Mole fraction HD	0.004	0.004	0.496	0.686	0.268
Mole fraction D_2	0.497	0.556	0.001	0.001	0.000
Excess free energy ΔG^E in cal/mole	1.65±0.8	1.15±0.5	0.80±0.4	0.70±0.3	0.80±0.4

most satisfactory methods of testing the predictions of the theory would be (a) to test the dependence of the excess molar quantities on the mole fractions of the components in the mixture and (b) to test the approximate law of corresponding states for mixtures of different isotopes. To test the dependence of the excess molar quantities on the mole fractions we require data, at fixed T and P (or V), and for various concentrations. On the other hand to test the law of corresponding states we require data on a number of solutions of different isotopes, again at fixed T and P (or V). Since we can form three binary solutions from H_2, D_2, and HD it is likely that a thorough study of solutions of these three isotopes will provide us with sufficient data with which to test the theory.

4. He^3-He^4 SOLUTIONS

There is now a variety of evidence which indicates that the properties of the two pure isotopes of helium, He^3 and He^4, are to a large extent dependent on the type of statistics obeyed by their atoms. For example the specific heats and hydrodynamical flow properties are very different, at least for all temperatures for which measurements are available. The theory that we developed in the last two sections was, however, based on the assumption that all the particles in the mixture under consideration obeyed Boltzmann statistics. We therefore cannot expect to apply the theory directly to solutions of He^3 and He^4 isotopes. However, just because of this fact we can say that any deviations of the properties of He^3-He^4 solutions from those predicted by the theory are likely to be due to the fact that He^3 and He^4 atoms obey quantum statistics rather than Boltzmann statistics. We must therefore consider what properties we should predict for He^3-He^4 solutions.

The two most important predictions of the theory are, first, that the excess free energy of mixing depends only on second and higher powers of the relative mass differences and second, that the excess free energy depends on the mole fractions through the factor x_1x_2. As we have already pointed out, the first prediction indicates that the excess molar quantities should be small, and this prediction was born out by the data we quoted on the hydrogen isotopes. Now it is easily seen that the excess free energy of a mixture of isotopes whose particles obey quantum statistics rather than classical statistics *depends on both zero and first order terms in the mass differences*. Consequently we should expect that the excess molar quantities will be much larger for this type of solution. However, as the temperature of the solution is raised the influence of the different types of quantum statistics will decrease and it is likely that at sufficiently high temperatures the excess molar quantities will become of the same order of magnitude as those found in mixtures of hydrogen isotopes. Unfortunately there appears to be very little data available on He^3-He^4 mixtures. The only data that extend to temperatures well above the λ temperature are those due to Weinstock, Osborne, and Abraham.[13] They found that the vapor pressure for a 20% mixture of He^3 in He^4 was 6%, 20%, and 80% greater than that for an ideal solution at temperatures of 3°K, 2°K, and 1.2°K respectively. These values are in good qualitative agreement with the ideas presented in the foregoing. They seem to indicate that at about 3°K the different types of quantum statistics have very little influence on the properties of He^3 and He^4 mixtures. A much more satisfactory method of determining the influence of quantum statistics on these solutions would be to test, at fixed temperature and pressure (or volume), the dependence of some excess molar quantity on the mole fractions. Unfortunately there is insufficient data to enable us to do this satisfactorily. However, Nanda[14] has analyzed the rather scanty data due to Sommers,[15] on He^3-He^4 solutions above the λ temperature. He assumed that at these temperatures the solutions obey the composition law we have derived in this paper. We should note that the theory we have developed definitely shows that the nonideality parameter $W[=\frac{1}{2}(\lambda_1-\lambda_2)^2Q]$ is a function of both T and V (or P). We consequently cannot expect to fit the available data with a temperature independent W. Unfortunately, Sommer's data does not extend to temperatures above 2.2°K[16] and it

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[13] Weinstock, Osborne, and Abraham, Phys. Rev. **77**, 400 (1950).

[14] V. S. Nanda, Phys. Rev. **97**, 571 (1955).

[15] H. S. Sommers, Phys. Rev. **88**, 113 (1952).

[16] In a recent issue of Zhur. Eksptl. i Teort. Fiz. **26**, No. 6 (1954). B. Eselson has published a large amoung of data on solutions ranging in concentration from 0.4% to 8.08% and from temperatures of 1.3°K to 3.2°K. Unfortunately his data disagrees both with that due to Sommers and with that due to Weinstock, Osborne, and Abraham. In particular he finds large negative deviations from ideality above the λ temperature and these deviations show no signs of decreasing at 3.0°K. This behavior also contradicts our theoretical predictions.

is doubtful whether our theory is applicable at temperatures as near the λ point as this. Nevertheless Nanda, found that the data leads to a fairly consistent value of W of 1.8 cals/mole. He also states that this value for W will account for the experimental data of Daunt and Tseng[17] on a 4% solution of He^3 in He^4. To check Nanda's calculations we have calculated W from Weinstock's data on a 20% solution and we find that this leads to a value of 2.0 cals/mole, at 2.2°K. Considering the uncertainty in the experimental measurements, this value can be considered to be in good agreement with Nanda's value.

When a He^3-He^4 solution is solidified by the application of pressure it is almost certainly correct to assume that the atoms become localized on lattice sites. Consequently, when we enumerate the states of the system it makes no difference whether we apply Fermi-Dirac or Bose-Einstein statistics to the particles. For in a localized system both methods of enumeration lead to the same result as that obtained by the application of Boltzmann statistics.[3,18] Our theory is therefore directly applicable to solid solutions of He^3 and He^4. Perhaps the best way to test the theory in this instance would be to measure some simple property, such as the velocity of sound or the specific heat at constant pressure. The dependence of both these quantities on the mole fractions can easily be calculated from the formula we have derived for ΔF^E. The predicted dependence can then be compared with that found experimentally.

So far our remarks have been entirely qualitative in nature. We shall now show how, in principle at least, a quantitative comparison can be made between the properties of a helium mixture and the properties of a hydrogen mixture. Let us consider Eq. (3.2)

$$\Delta F^E/c(x,\lambda)=Q(m_0,T,V). \qquad (4.1)$$

We know from De Boer's work on the law of corresponding states[2] that the partition function Z depends only on the reduced variables T^*, V^*, and the parameter Λ^*. Here $T^*=kT/\epsilon$, $V^*=V/N\sigma^3$ and $\Lambda^*=h/\sigma(m\epsilon)^{\frac{1}{2}}$, where ϵ, σ, m have the usual significance. If we use the same methods as De Boer then we can easily show that $Q^*=Q/N\epsilon$, is also a function of T^*, V^*, and Λ^* alone. Therefore if we set $(\Delta F^E)^*=\Delta F^E/N\epsilon$, we can write Eq. (4.1) in the form

$$(\Delta F^E)^*/c(x,\lambda)=Q^*(T^*,V^*,\Lambda_0^*). \qquad (4.2)$$

We now consider two different mixtures; (i) a mixture of hydrogen isotopes and (ii) a mixture of He^3 and He^4. Let us choose reference masses m_{01} for the first and m_{02} for the second. Then if we make the assumption that the atoms and molecules of all the isotopes in the two mixtures obey Boltzmann statistics we can write down two equations similar to Eq. (4.1), namely,

$$(\Delta F^E)_1^*/c(x,\lambda)=Q^*(T^*,V^*,\Lambda_{01}^*), \qquad (4.3)$$

and

$$(\Delta F^E)_2^*/c(x',\lambda')=Q^*(T^*,V^*,\Lambda_{02}^*), \qquad (4.4)$$

where x, λ refer to the hydrogen mixture, x', λ' refer to the helium mixture, and Λ_{01}^* and Λ_{02}^* are the appropriate values of Λ^*. Clearly the two functions on the right hand sides of Eqs. (4.3) and (4.4) will become identical if we chose m_{01} and m_{02} so that $\Lambda_{01}^*=\Lambda_{02}^*$. This implies that m_{01} and m_{02} must satisfy the equation,

$$m_{01}/m_{02}=(\epsilon_2/\epsilon_1)(\sigma_2/\sigma_1)^2\simeq 0.2. \qquad (4.5)$$

The numerical value was obtained by substituting the known[19] values of ϵ_1, ϵ_2, σ_1, and σ_2. When this condition is fulfilled we can write,

$$(\Delta F^E)_1^*/c(x,\lambda)=(\Delta F^E)_2^*/c(x',\lambda'), \qquad (4.6)$$

where of course $(\Delta F^E)_1^*$ and $(\Delta F^E)_2^*$ are to be regarded as a function of the reduced variables T^* and V^*. It is obvious from this last equation that a similar equation must hold between the reduced values of any other property of the two mixtures. In fact this equation merely expresses a general, though approximate, law of corresponding states between the properties of mixtures of isotopes of different substances; it can be regarded as a generalization of the more restricted law that we discussed in the last section. The reason why we are able to set up a law of corresponding states between the properties of quantum mechanical systems is that we have considerable freedom in the choice of the reference masses and m_{01} and m_{02}. As long as we chose them so that Eq. (4.5) is satisfied the above law will hold.

We can now use Eq. (4.5) to predict the properties of He^3-He^4 solutions from those of a hydrogen mixture. Let us suppose that we have measured a reduced excess quantity, $(\Delta X)_1^*$, as a function of T^* and P^* for a hydrogen mixture. Then we have at once that $(\Delta X)_2^*$ for a He^3-He^4 solution is given by

$$(\Delta X)_2^*=[c(x',\lambda')/c(x,\lambda)](\Delta X)_1.^* \qquad (4.7)$$

But this prediction is only possible if we assume that the atoms or molecules of all the substances obey Boltzmann statistics. We can therefore say that any departures of $(\Delta X)_2^*$ from that predicted by the above equation are almost certain to be due to the different types of quantum statics obeyed by the He^3 and He^4 atoms. Equation (4.7) and other similar equations therefore enable us to determine, in principal at least, the influence of quantum statistics on the properties of He^3-He^4 solutions.

We must now consider whether such a comparison can be carried through in practice. There are two points to be considered in this connection. Firstly, Eq. (4.1)

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[17] J. G. Daunt and T. P. Tseng (unpublished).

[18] This fact suggests that there may be a marked decrease in the deviations from ideal behavior of He^3-He^4 solutions as they solidify. It is also likely that the dependence of ΔF^E on the mole fractions will change as the solution solidifies.

[19] J. De Boer, Repts. Progr. Phys. 12, 305 (1948).

will be an accurate approximation as long as m_{01} and m_{02} are chosen so that (a) Eq. (4.5) is satisfied and (b) so that the relative mass differences λ and λ' for the two mixtures are as small as possible. The largest value of m_{02} would therefore appear to be about 5 amu, with this value λ_1' and λ_2' are $\frac{2}{3}$ and $\frac{1}{4}$, respectively. If m_{02} is about 5 amu then m_{01} must be about 1 amu to satisfy Eq. (4.5). We then find that for a H_2-HD mixture, λ_1 and λ_2 are $-\frac{1}{2}$ and $-\frac{2}{3}$, respectively. While these values are rather large it is unlikely that they are so large as to render the theory inapplicable. Secondly, if we wish to make an exact comparison between the properties of the two mixtures then the reduced thermodyhamic variables must have the same values. For example, if we consider properties under conditions of constant pressure and temperature then we must have $T_1^*=T_2^*$ and $p_1^*=p_2^*$. Using the known values of ϵ_1, ϵ_2, σ_1, and σ_2 we find that this means that $T_1=3.7T_2$ and $p_1=2.5p_2$. It should be a simple matter to fulfill these two conditions.

5. COMPARISON WITH PRIGOGINE'S THEORY

In a series of interesting papers[7–9] (hereafter referred to as I, II, and III) Prigogine has developed an approximate theory of solutions of isotopes. Papers I and II are concerned with the thermodynamic properties of mixtures of isotopes at absolute zero. The assumptions are made that the particles of the mixture are localized on lattice points and that they are coupled by means of harmonic forces. It is, of course, impossible to solve even this simple problem completely, except in the one dimensional case.[20] Prigogine therefore treats the three-dimensional case by means of perturbation theory. He finds that the first-order terms in the mass differences do not contribute to the energy of mixing and that the second order term is always as positive. This latter result leads at once to the prediction of a phase separation of the isotopes at some temperature above absolute zero. Both of these results are in complete agreement with our own; namely (ii) and (iii) of Sec. III. However, on the basis of these assumptions the energy of mixing is found to be only about 10^{-1} cal/mole. That is to say it is about ten times smaller than that found in mixtures of hydrogen isotopes. As Prigogine points out, this large discrepancy is almost certainly due to the very large anharmonic forces that come into play because of the higher zero point energy of these substances.

In paper III, Prigogine introduces a new assumption. This is that if by means of suitable external pressures we make the molar volumes of the components equal to that of the mixture then the free energy of the mixture should be equal to that of the components, apart from the usual configurational entropy term. This means that before we mix the two components we must apply a suitable positive pressure to one a negative pressure to the other. With this assumption the free energy of the mixture, $f_m(T,v)$, is given by the equation,

$$f_m(T,v)=x_1f_1(T,v)+x_2f_2(T,v)-RT\sum_{i=1,2}x_i\log x_i, \quad (5.1)$$

where $f_i(T,v)$ is the free energy of the ith component at a temperature T and molar volume v. If we expand each of the f_i in Eq. (5.1) in a Taylor series in powers of $(v-v_i)$ and substitute these expansions into the above expression for f_m then we can easily relate the properties of the mixture to those of its components. The principal results that follow from this treatment are as follows:

(a) The excess free energy is proportional to $(v_1-v_2)^2$, when terms of order $(v-v_i)^3$ are neglected, and is always positive. Again we should expect a phase separation of the isotopes. This result is in agreement with our own conclusions.

(b) The numerical value for the excess free energy is in good agreement with the experimental values derived from the data due to Hoge and Arnold.[13]

(c) The excess free energy is not a symmetrical function of the mole fractions x_1 and x_2. This result therefore is different from our own and consequently can be used to compare the two theories experimentally.

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[20] F. J. Dyson, Phys. Rev. 92, 1331 (1954).