Statistical Mechanics of Mixtures of BoseEinstein and FermiDirac Systems

William Band

Additional information on J. Chem. Phys.

If this is also valid for the mixed solvent, and if cation solvation in the mixture is primarily by water molecules, it is possible to give a qualitative if not too convincing explanation of the effect.

It is easy to show that for saturated NaCl and KCl solutions in 50-mole percent methanol, the thermodynamic potential of the methanol is an increasing function of salt concentration and that of the water a decreasing function.[14] If

[14] Denoting methanol, water, and salt by 1, 2, and s, respectively, and noting that in saturated solution the potential of the salt μ_s must be constant, it follows that for constant temperature and pressure

$$(\partial \mu_s/\partial n_s)_{n_1, n_2} \cdot dn_s + (\partial \mu_s/\partial n_1)_{n_2, n_s} \cdot dn_1 = 0, \quad (A)$$

$$(\partial \mu_1/\partial n_s)_{n_1, n_2} = (\partial \mu_s/\partial n_1)_{n_2, n_s}$$
$$= -(\partial \mu_s/\partial n_s)_{n_1, n_2} \cdot (dn_s/dn_1)_{n_2}. \quad (B)$$

If from Akerlof and Turck's data (J. Am. Chem. Soc. **57**, 1746 (1935)) moles of salt per mole of solvent in the saturated solutions be plotted against methanol mole fraction of the solvent, and if the tangent at 0.5-mole fraction be produced, its intersection with the ordinate at $N_1 = 1$ is obviously $(dn_s/dn_1)_{n_2}$. The intercept is -0.017 and -0.015 for NaCl and KCl, respectively; but $(\partial \mu_s/\partial n_s)_{n_1, n_2}$ is inherently positive; hence $(\partial \mu_1/\partial n_s)_{n_1, n_2}$

increasing electrolyte concentration has the same effect in dilute solutions as in saturated, and if there be an equilibrium between water molecules organized around the cations and the "free" water molecules in the solution, increase in salt concentration should decrease cation hydration, thus resulting in a decrease in diameter of the hydrated complex and an increase, for this reason, of cation mobility in comparison with anion. If a varying degree of preferential cation solvation with one solvent constituent be the explanation, as suggested above, it is a further argument against the use of mixed solvents in studies of ionic transport.

is also positive, i.e., the potential of the methanol is an increasing function of salt concentration in saturated (or nearly saturated) solution. Similarly, from the Gibbs-Duhem equation, it follows (T, P, n_1, n_2 constant) that

$$-n_2 \cdot \partial \mu_2/\partial n_s = n_1 \cdot \partial \mu_1/\partial n_s + n_s \cdot \partial \mu_s/\partial n_s. \quad (C)$$

Thus for saturated or nearly saturated solution, the potential of the water must be a decreasing function of salt concentration, since both items on the right of Eq. (C) are positive.

Statistical Mechanics of Mixtures of Bose-Einstein and Fermi-Dirac Systems

WILLIAM BAND

Institute for Nuclear Studies, The University of Chicago, Chicago, Illinois

(Received December 29, 1947)

Full quantum corrections are applied to Mayer's recent extension of statistical thermodynamics to the multi-component liquid phase. The resulting formulae are too general in nature to permit quantitative interpretation, but qualitatively, in the case of Bose-Einstein systems, the theory predicts a typical lambda-point condensation in momentum space. A Fermi-Dirac isotopic component dissolved to small concentrations in a Bose-Einstein liquid phase, like He_3 in He_4, is shown to behave to a first approximation independently of the Bose-Einstein degeneracy of the solvent at all temperatures above the lambda-point. The theory appears unable to handle the situation below the lambda-point.

1. INTRODUCTION

THIS paper presents a first attempt to apply Mayer's recent extensions of statistical thermodynamics[1] to the problem of the Bose-Einstein lambda-transition in liquid systems. Following the work of McMillan and Mayer[2] on multi-component systems, it is possible to

develop the theory so as to include any kind of mixture, and incidentally it is shown how the theory can be used to discuss the behavior of a Fermi-Dirac isotopic component dissolved to small concentrations in a Bose-Einstein liquid like He_3 in He_4.

The existence of the lambda-transition in a pure Bose-Einstein liquid can be qualitatively explained by this theory, but it does not seem possible to obtain information by its means con-

[1] J. E. Mayer, J. Chem. Phys. **10**, 629–643 (1942).
[2] W. G. McMillan and J. E. Mayer, J. Chem. Phys. **13**, 276–305 (1945).

cerning the behavior of the system below the lambda temperature. Moreover, any purely statistical approach to the behavior of the Bose-Einstein liquid below the lambda-temperature must overcome the difficulty pointed out by Schiff,[3] namely that the population of the lowest state becomes theoretically so much greater than that of the other states that the approximations generally involved in the basic theorems of statistical mechanics become invalid. While attempts to solve the problem of the condensed phase in terms of quantum hydrodynamics (Landau,[4] Tisza[5]) may not be without interest, it seems that the correct method of attack is to improve the basic theorems of the statistical mechanics, perhaps as suggested by Born and Green.[6] Into this question we shall not enter here. For a review of earlier work the reader may refer to a thesis by J. de Boer[7] on the theory of compressed gases.

2. QUANTUM CORRECTIONS FOR THE DISTRIBUTION FUNCTIONS

To handle multi-component systems we use a modification of the symbolism introduced by McMillan and Mayer.[2] Let the energy of the whole system be $E_N(\{\mathbf{N}\}_p, \{\mathbf{N}\}_q)$ or $E_N(\{\mathbf{N}\}_{pq})$ where N is the total number of particles, $\mathbf{N}$ is the set of numbers of particles in all the components, $N_1, N_2, \cdots, \{\mathbf{N}\}_q$ the coordinates of these particles, and $\{\mathbf{N}\}_p$ their momenta. The partition function of the system is Q_N where, writing the sum over the momenta in the form of an integral,

$$\prod_{s,a}[N_s!h^{3N_s}N_a!h^{3N_a}]Q_N$$

$$= \int \cdots \int \exp[-E_N(\{\mathbf{N}\}_{pq})/kT]d\{\mathbf{N}\}_{pq}. \quad (2.1)$$

Here $\prod_s$ means product over all the components with symmetric statistics (Bose-Einstein), and $\prod_a$ the product over all antisymmetric components (Fermi-Dirac). In particular

$$\sum_s N_s + \sum_a N_a = N.$$

[3] L. I. Schiff, Phys. Rev. 59, 751, 758 (1941).
[4] L. Landau, J. Phys. U.S.S.R. 5, 71-90 (1941); 8, 1-3 (1944); 11, 91 (1947).
[5] L. Tisza, J. de Physique 8, 350 (1940).
[6] M. Born and H. S. Green, Nature 159, 738 (1947).
[7] J. de Boer, "Contribution to the Theory of Compressed Gases," Amsterdam, Thesis (1940).

The complete wave function for the whole system in the limit of zero intermolecular forces is

$$\phi_N(\{\mathbf{N}\}_{pq}) = \prod_s \frac{1}{N_s!V^{\frac{1}{2}N_s}}\mathcal{P}_{tu}\exp\left[\frac{2\pi i}{h}(\mathbf{p}_{st}\cdot\mathbf{q}_{su})\right]$$

$$\times \prod_a \frac{1}{N_a!V^{\frac{1}{2}N_a}}\mathfrak{D}_{tu}\exp\left[\frac{2\pi i}{h}(\mathbf{p}_{at}\cdot\mathbf{q}_{au})\right] \quad (2.2)$$

where $\mathcal{P}_{tu}$ means the "permanent" formed of all elements indicated by the suffixes t,u taken over the B.E. type particles in the component indicated by the suffix s; and $\mathfrak{D}_{tu}$ means the determinant formed of the indicated elements. $\mathbf{p}_{st}$ means the momentum vector of the tth particle of the sth component, $\mathbf{q}_{au}$ the position vector of the uth particle of the sth component, and so on.

The presence of classical interaction can be treated as a perturbation, and the perturbed wave functions expressed as linear combinations of the above ϕ_N's for different energy (momentum) states:

$$\prod_{s,a}[N_s!h^{3N_s}N_a!h^{3N_a}]\psi_N(\{\mathbf{N}\}_{pq})$$

$$= \int \cdots \int a_N(\{\mathbf{N}\}_{pp'})\phi_N(\{\mathbf{N}\}_{p'q})d\{\mathbf{N}\}_{p'}. \quad (2.3)$$

The distribution (probability) functions normalized to V^N are

$$F_N\{\mathbf{N}\}_q \equiv \frac{V^N}{h^{3N}Q_N\prod_{s,a}N_s!N_a!}\int \cdots \int \psi_N^*(\{\mathbf{N}\}_{pq})$$

$$\times \exp[-E_N(\{\mathbf{N}\}_{pq})/kT]$$

$$\times \psi_N(\{\mathbf{N}\}_{pq})d\{\mathbf{N}\}_p, \quad (2.4)$$

and because the coefficients $a_N(\{\mathbf{N}\}_{pp'})$ are orthogonal, this reduces to

$$F_N\{\mathbf{N}\}_q \equiv \frac{V^N}{h^{3N}Q_N\prod_{s,a}N_s!N_a!}\int \cdots \int \phi_N^*(\{\mathbf{N}\}_{pq})$$

$$\times \exp[-E_N(\{\mathbf{N}\}_{pq})/kT]$$

$$\times \phi_N(\{\mathbf{N}\}_{pq})d\{\mathbf{N}\}_p. \quad (2.5)$$

In this equation it is to be remembered that the exponential factor in the integrand is an operator acting on ϕ_N. It has been shown that, in the case of a single component system in classical sta-

tistics (Kirkwood,[8] Mayer and Band[9])

$$\exp[-E_N(\mathbf{p},\mathbf{r})/kT]\phi_N(\mathbf{p},\mathbf{r})$$
$$=\phi_N(\mathbf{p},\mathbf{r})\exp[-E_N^*(\mathbf{p},\mathbf{r})/kT],$$

where E_N^* is a quantity that differs from the result of operating with E_N upon unity only by terms which may be neglected in a first approximation (which is quite good in all cases met with in the present class of problems).* The same statement is equally true for the symmetrized wave functions appropriate either to Bose-Einstein or to Fermi-Dirac statistics, and the general case of mixed multi-component systems can be included. This is because, although the energy E_N includes the classical interactions between particles of all types, the theorem does not depend on the form of the potential energy as a function of the coordinates. Thus we write to a good approximation:

$$F_N\{\mathbf{N}\}_q = \frac{V^N}{h^{3N}Q_N\prod_{s,a}N_s!N_a!}\int\cdots\int\phi_N^*(\{\mathbf{N}\}_{pq})$$

$$\times\phi_N(\{\mathbf{N}\}_{pq})\exp\left[\frac{-E_N^*(\{\mathbf{N}\}_{pq})}{kT}\right]d\{\mathbf{N}\}_p \quad (2.6)$$

where E_N^* differs from the total energy by a negligible quantity. This expression can now be integrated and we obtain

$$F_N\{\mathbf{N}\}_q = \frac{V^N\exp[-U_N\{\mathbf{N}\}_q/kT]}{\int\cdots\int\exp[-U_N\{\mathbf{N}\}_q/kT]d\{\mathbf{N}\}_q}$$

$$\times\prod_s \mathcal{O}_{tu}\exp\left[-\frac{\pi}{\lambda_s^2}q_{stu}^2\right]$$

$$\times\prod_a \mathfrak{D}_{tu}\exp\left[-\frac{\pi}{\lambda_a^2}q_{atu}^2\right], \quad (2.7)$$

[8] J. G. Kirkwood, Phys. Rev. **44**, 31 (1933).
[9] J. E. Mayer and W. Band, J. Chem. Phys. **15**, 141 (1947).

* It may be supposed that because the neglected series of terms will diverge at low enough T (Reference 7, p. 15), the expression can no longer be used at liquid helium temperatures. Actually, however, the ratio of successive terms is of the order $h^2/8\pi^2 mkT\lambda^2$, where λ is a length comparable to the mean free path of an atom. Taking $\lambda=10^{-7}$ cm, this ratio for helium is still only 0.06 even at $T=1^\circ$K, so the neglected series is still really small.

where

$$\lambda_s^2\equiv\frac{h^2}{2\pi m_s kT}, \quad \lambda_a^2\equiv\frac{h^2}{2\pi m_a kT}, \quad (2.8)$$

m_s, m_a being the masses of the particles of the B.E. and F.D. components respectively, and q_{stu}^2 means the square of the distance between the particles t,u in the s component, etc. $U_N\{\mathbf{N}\}_q$ is the total potential energy as a function of all the coordinates of all the particles. For convenience we shall write the degeneracy factors:

$$\mathcal{O}_{tu}\exp\left[-\frac{\pi}{\lambda_s^2}q_{stu}^2\right]\equiv B_s\{N_s\}_q, \quad (2.9)$$

$$\mathfrak{D}_{tu}\exp\left[-\frac{\pi}{\lambda_a^2}q_{atu}^2\right]\equiv B_a\{N_a\}_q, \quad (2.10)$$

and express (2.7) as

$$F_N\{\mathbf{N}\}_q = F_N\{\mathbf{N}\}_q{}_{\text{Class}}$$

$$\times\prod_s B_s\{N_s\}_q\prod_a B_a\{N_a\}_q. \quad (2.11)$$

3. SERIAL EXPANSIONS FOR THE DEGENERACY FACTORS

To handle this, we introduce the notation of Mayer and Montroll[10] and in addition let the symbol $\sum\{k_s\{n_i^*\}N_s\}_u$ indicate the sum over all values of k_s, where the N_s particles have been partitioned into k_s unconnected subsets $n_1, n_2\cdots n_{k_s}$ each $n_1\geqslant 2$ in such a way as to include every member of the set of N_s particles in some subset. Without the asterisk the symbol will not require that the partitioning shall include every member in subsets of size 2 or larger, but will permit free particles that do not enter the expression. With this understanding we can write

$$B_s\{N_s\}_q = \sum\{k_s\{n_i\}N_s\}_u\prod_{i=1}^{k_s}g_s\{n_i\}_q \quad (3.1)$$

where each factor

$$g_s\{n_i\}_q\equiv\exp\left[-\frac{\pi}{\lambda_s^2}(q_{12}^2+q_{23}^2+\cdots q_{n_i1}^2)\right] \quad (3.2)$$

is a product of factors taken over the closed cycle of particles n_i in number. The sum in (3.1) evidently contains the terms arising only from

[10] J. E. Mayer and E. Montroll, J. Chem. Phys. **9**, 2–16 (1941).

such permutations as, e.g.

$$1234 \cdots N-1 \; N$$
$$1324 \cdots N-1 \; N$$

namely $\exp[-(\pi/\lambda^2)(q_{23}{}^2+q_{32}{}^2)]$. The factors from $q_{11}{}^2$, etc., reduce to unity. No factor such as $\exp[-(\pi/\lambda^2)q_{23}{}^2]$ can occur without its associated factor $\exp[-(\pi/\lambda^2)q_{32}{}^2]$. We express (3.1) in the form

$$B_s\{N_s\}_q = \sum\{M_s\}N_s \sum\{k_s\{m_i{}^*\}M_s\}_u$$
$$\prod_{i=1}^{k_s} g_s\{m_i\}_q, \quad (3.3)$$

where $\sum\{M_s\}N_s \sum\{k_s\{m_1{}^*\}M_s\}_u$ is an abbreviation for the operation of collecting together all the products of the g_s's that include all the particles in some subset $\{M_s\}$ of N_s and no others, and summed over all subsets $\{M_s\}$ in N_s. For example, terms like $\exp[-(\pi/\lambda^2)(q_{12}{}^2+q_{21}{}^2)]$ will appear in the subset $\{2\}$ and not in any larger ones.

Write

$$B_s{}^*\{M_s\}_q \equiv \sum\{k_s\{m_i{}^*\}M_s\}_u \prod_{i=1}^{k_s} g_s\{m_i\}_q, \quad (3.4)$$

so that
$$B_s\{N_s\}_q = \sum\{M_s\}N_s B_s{}^*\{M_s\}_q. \quad (3.5)$$

It will be found necessary to integrate this series over the coordinates:

$$\int \cdots \int B_s\{N_s\}_q d\{N_s\}_q$$
$$= \sum\{M_s\}N_s \int \cdots \int B_s{}^*\{M_s\}_q$$
$$\times d\{N_s-M_s\}_q d\{M_s\}_q \quad (3.6)$$

or, recalling the number of subsets $\{M_s\}$ in N_s:

$$\int \cdots \int B_s\{N_s\}_q d\{N_s\}$$
$$= \sum_{M_s} \frac{N_s! V^{N_s-M_s}}{M_s!(N_s-M_s)!} \sum\{k_s\{m_i{}^*\}M_s\}_u$$
$$\times \prod_{i=1}^{k} \int \cdots \int g_s\{m_i\}_q d\{m_i\}_q. \quad (3.7)$$

This can be rewritten in a more familiar notation. Let the k_s subsets $\{m_i\}$ in $\{M_s\}$ contain σ_l subsets of l particles each so that $k_s = \sum_l \sigma_l$

and $M_s = \sum_l l\sigma_l$ then

$$\sum\{k_s\{m_i{}^*\}M_s\}_u \prod_{i=1}^{k_s} \int \cdots \int g_s\{m_i\}_q d\{m_i\}_q$$
$$= M_s! \sum_{\sigma_l} \prod_l \frac{1}{\sigma_l!}[VI_{sl}]^{\sigma_l} \quad (3.8)$$

where

$$lVI_{sl} \equiv \int \cdots \int g_s\{l\}_q d\{l\}_q. \quad (3.9)$$

The factor l appearing in (3.9) disappears from (3.8) because of the l-fold duplication of each cycle that appears only once on the left side of (3.8). Finally, then

$$\int \cdots \int B_s\{N_s\}_q d\{N_s\}_q = N! \sum_{M_s} \frac{V^{N_s-M_s}}{(N_s-M_s)!}$$
$$\times \sum_{\sigma_l} \prod_l \frac{1}{\sigma_l!}[VI_{sl}]^{\sigma_l} [\sum_l l\sigma_l = M_s]. \quad (3.10)$$

The value of the integral (3.9) is known to be[7]

$$I_{sl} = \lambda^{3(l-1)}/l^{5/2}. \quad (3.11)$$

Using the same notations as above, in the Fermi-Dirac case we write

$$B_a\{N_a\}_q = \sum\{k_a\{n_i\}N_a\}_u$$
$$\times \prod_{i=1}^{k_a}(-1)^{[n_l-1]}g_a\{n_i\}_q, \quad (3.12)$$

where $[n_i-1]$ represents one less than the number of non-diagonal factors in the determinant. This alternating sign carries right through the above argument and leads finally to

$$\int \cdots \int B_a\{N_a\}_q d\{N_a\}_q = \sum_{M_a} \frac{N_a! V^{N_a-M_a}}{M_a!(N_a-M_a)!}$$
$$\times \sum\{k_a\{m_i{}^*\}M_a\}_u \prod_{s=1}^{k_a}(-1)^{[m_i-1]}$$
$$\times \int \cdots \int g_a\{m_i\}_q d\{m_i\}_q, \quad (3.13)$$

and

$$\int \cdots \int B_a\{N_a\}_q d\{N_a\}_q = N_a! \sum_{M_a} \frac{V^{N_a-M_a}}{(N_a-M_a)!}$$
$$\times \sum_{\sigma_l} \prod_l (-1)^{l-1}\frac{1}{\alpha_l}[VI_{al}]^{\alpha_l}, \quad (3.14)$$

where
$$I_{al} = \lambda_a{}^{3(l-1)}/l^{5/2}. \quad (3.15)$$

4. THE FUNDAMENTAL THEOREMS

In the present problem we can write out the grand partition function theorem in the following form:

$$\exp[VP(\mathbf{z})/kT] = \sum_{\mathbf{N}} \prod_{x=s,a} (z_x^{N_x}/N_x!)$$

$$\times \int \cdots \int F\{N_x\}d\{N_x\}, \quad (4.1)$$

where $\mathbf{z}$ represents the set of fugacities z_s and z_a, all s and a. From this point on there are no momentum variables, so we drop the q suffix from the bracket notation, and revert to the notation used by McMillan and Mayer. Recalling that these distribution functions occurring in (4.1) are defined at zero fugacity, and that they combine as probabilities, we may write (4.1) in the form:

$$\exp[VP(\mathbf{z})/kT] = \sum_{\mathbf{N}} \prod_{x=s,a} (z_x^{N_x}/N_x!)$$

$$\times \int \cdots \int F(\mathbf{o}, \{\mathbf{N}\})d\{\mathbf{N}\}, \quad (4.3)$$

or, using (2.11):

$$\exp[VP(\mathbf{z})/kT] = \sum_{\mathbf{N}} \int \cdots \int \prod_{x=s,a} \frac{z_x^{N_x}}{N_x!}$$

$$\times B_x\{N_x\} F_{\text{Class}}(\mathbf{o}, \{\mathbf{N}\})d\{\mathbf{N}\}. \quad (4.4)$$

Mayer's generalized grand partition function theorem relating the properties of the assembly at two different fugacity sets $\mathbf{z}+\mathbf{y}$ and $\mathbf{z}$, where $\mathbf{z}$ can be such as to place some or all of the components in the liquid phase, can be written as

$$\exp[VP(\mathbf{z}+\mathbf{y})/kT]$$

$$\times \prod_{x=s,a} \left[\left\{\frac{\rho_x(y_x+z_x)}{y_x+z_x}\right\}^{N_x}\right] F(\mathbf{y}+\mathbf{z}, \{\mathbf{N}\})$$

$$= \sum_{\mathbf{M}} \prod_{x=s,a} \left[\frac{y_x^{M_x}}{M_x!}\left\{\frac{\rho_x(z_x)}{z_x}\right\}^{N_x+M_x}\right] \exp[VP(\mathbf{z})/kT]$$

$$\times \int \cdots \int F(\mathbf{z}, \{\mathbf{N}+\mathbf{M}\})d\{\mathbf{M}\}. \quad (4.5)$$

Here ρ_s, ρ_a are the numerical densities (concentrations) of the symmetrical and antisymmetrical components at the indicated fugacities. A rather more symmetrical form of this law is obtained if we multiply each side of (4.5) by $\prod_{s,a} y_s^{N_s} y_a^{N_a}$ and integrate over all coordinates $\prod_{s,a} d\{N_s\}d\{N_a\} \equiv d\{N\}$ and sum over all subdivisions of the set $\{N_a+M_a\}$ into $\{N_a\}$ and $\{M_a\}$ and of the set $\{N_s+M_s\}$ into $\{N_s\}$ and $\{M_s\}$. The result is

$$\sum_{\mathbf{N}} \exp[VP(\mathbf{y}+\mathbf{z})/kT]$$

$$\times \prod_{x=s,a} \left[\frac{1}{N_x!}\left\{\frac{\rho_x(y_x+z_x)}{y_x+z_x}\right\}^{N_x}\right]$$

$$\times \int \cdots \int F(\mathbf{y}+\mathbf{z}, \{\mathbf{N}\})d\{\mathbf{N}\}$$

$$= \sum_{\mathbf{N}} \exp[VP(\mathbf{z})/kT]$$

$$\times \prod_{x=s,a} \left[\frac{1}{N_x!}\left\{\frac{y_x\rho_x(z_x)}{z_x}\right\}^{N_x}\right]$$

$$\times \int \cdots \int F(\mathbf{z}, \{\mathbf{N}\})d\{\mathbf{N}\}. \quad (4.6)$$

The expansion of the distribution functions in terms of irreducible integrals is formally identical with that given by McMillan and Mayer[11] but we must remember that the presence of the degeneracy factors alters the meaning of the irreducible integrals. Also it is worth noting that because of this, the distribution functions do not reduce to the familiar forms in terms of potential energy, and the potentials of average force do not approach the classical potential energies even at zero fugacity.

5. MIXTURES OF PERFECT GASES

Here, by definition, the value of F_{Class} is constant unity, so the grand partition function becomes simply

$$\exp[VP(\mathbf{z})/kT]$$

$$= \sum_{\mathbf{N}} \sum_{x=s,a} \int \cdots \int \frac{z_x^{N_x}}{N_x!} B_x\{N_x\}d\{N_x\}. \quad (5.1)$$

Using (3.10) and (3.14) here leads easily to the result

$$VP(\mathbf{z}) = kT\left[\sum_s \sum_{l \geqslant 1} VI_{sl}z_s^l\right.$$

$$\left. + \sum_a \sum_{l \geqslant 1} (-1)^{l-1} VI_{al}z_a^l\right], \quad (5.2)$$

[11] See reference 2, Eq. (54).

if we conventionally write $I_{s1}=I_{a1}=1$, all s, a. By (3.11) and (3.15) we then have

$$P(\mathbf{z}) = kT \sum_{l \geqslant 1} \left[\sum_s \frac{1}{\lambda_s^2} (\lambda_s^3 z_s)^l / l^{5/2} \right.$$

$$\left. + \sum_a \frac{1}{\lambda_a^3} (\lambda_a^3 z_a)^l (-1)^{l-1} / l^{5/2} \right]. \quad (5.3)$$

Evidently the law of partial pressures is still valid so long as none of the components reaches the lambda-point where $z_s = 1/\lambda_s^3$, the critical concentration being $\rho_s = (1/\lambda_s^3) \sum_l (1/l^{\frac{5}{2}})$. The presence of other uncondensed components does not alter the transition temperature of this lambda-transition, but what happens to the uncondensed components after the first one has undergone the Bose-Einstein condensation cannot be ascertained.

6. MIXTURES OF IMPERFECT GASES

The exact treatment of imperfect gases demands an integration of the distribution functions, and this can be carried out formally in precisely the same way as was done for the classical functions by McMillan and Mayer.[2] The resulting equations are so general in nature, however, as to be practically meaningless because the irreducible integrals do not have the simple interpretations possible in the classical case. We therefore find it expedient to approach the problem with somewhat less rigor, and consider two different limiting forms: (a) the gas is highly imperfect but the quantum degeneracy small enough to be regarded as a perturbation, and (b) the quantum degeneracy is treated exactly while the gas imperfections are regarded as small perturbations.

The point of departure in case (a) is the general theorem given by McMillan and Mayer,[12] which we write here as

$$F(\mathbf{z}, \{\mathbf{N}+\mathbf{M}\}) = F(\mathbf{z}, \{\mathbf{N}\}) \sum \{k\{m_i\}\mathbf{M}\}_u$$

$$\times \prod_{i=1}^k \{f_m^*(\mathbf{z}, \{m_i\}\mathbf{M})$$

$$+ \sum_{\{n\}N} f_{nm}^*(\mathbf{z}, \{n\}\mathbf{N}, \{m\}\mathbf{M})\}. \quad (6.1)$$

The cluster functions f_m^*, f_{nm}^* are different from their classical counterparts only because of the

---

[12] See reference 2, Eq. (51).

degeneracy factors present in the distribution functions in terms of which they are defined. If, however, the quantum degeneracy is small, the degeneracy factors can be treated as separable so that we can write (6.1) approximately as

$$F(\mathbf{z}, \{\mathbf{N}+\mathbf{M}\}) = F(\mathbf{z}, \{\mathbf{N}\}) \prod_{x=s,a} B_x\{M_x\}$$

$$\times \sum \{k\{m_i\}\mathbf{M}\}_u \prod_{i=1}^k \{f_m(\mathbf{z}, \{m_i\}\mathbf{M})$$

$$+ \sum_{\{n\}N} f_{nm}(\mathbf{z}, \{n\}\mathbf{N}, \{m\}\mathbf{M})\}, \quad (6.2)$$

where the functions f_m and f_{nm} are now the classical ones. We now make use of (3.1) and (3.12) and note that because the degeneracy factors are only non-negligible where clusters are present, we can write (6.2) as

$$F(\mathbf{z}, \{\mathbf{N}+\mathbf{M}\}) = F(\mathbf{z}, \{\mathbf{N}\}) \sum \{k\{m_i\}\mathbf{M}\}_u$$

$$\times \prod_{x=s,a} \left[\prod_{j=1}^{k_x} g_x(\{n_j\}m_i)(-1)^{(n_j-1)\delta_{xa}} \right]$$

$$\times \{f_m(\mathbf{z}, \{m_i\}\mathbf{M})$$

$$+ \sum_{\{n\}N} f_{nm}(\mathbf{z}, \{n\}_N, \{m\}_M)\}, \quad (6.3)$$

the degeneracy g-factors involve only subsets of the sets occurring in the cluster functions f_n.

This can now be integrated over $d\{\mathbf{M}\}$ to give formally the same result as classically:

$$\int \cdots \int F(\mathbf{z}, \{\mathbf{N}+\mathbf{M}\}) d\{\mathbf{M}\}$$

$$= F(\mathbf{z}, \{\mathbf{N}\}) \prod_{s,a} M_s! M_a! \sum_{\mu_m}$$

$$\times \prod_m \frac{1}{\mu_m!} \{Vb_m^*(\mathbf{z}) + \sum_{\{n\}N} b_{nm}^*(\mathbf{z}, \{n\}N)\}^{\mu_m}, \quad (6.4)$$

where now, however,

$$V[\prod_{s,a} m_s! m_a!] b_m^*(\mathbf{z})$$

$$\equiv \int \cdots \int \prod_{x=s,a} \left[\sum \{k_x\{n_j\}m_x\}_u \right.$$

$$\times \prod_{j=1}^{k_x} (-1)^{[n_j-1]\delta_{xa}} g_x(\{n_j\}m_x) \right]$$

$$\times f_m(\mathbf{z}, \{m\}M) d\{m\}, \quad (6.5)$$

$\{m_s\}$ and $\{m_a\}$ being the B.E. and the F.D. subsets in $\{\mathbf{m}\}$, and a similar definition for

$$b_{nm}^* \text{ in terms of } f_{nm}. \quad (6.6)$$

In terms of these modified integrals the pressure equation is of the same form as classically.[13] The same reasoning from the generalized grand partition function gives

$$P(\mathbf{z}+\mathbf{y}) - P(\mathbf{z})$$

$$= kT \sum_m b_m{}^*(\mathbf{z}) \prod_{x=s,a} \left\{ \frac{y_x \rho_x(z_x)}{z_x} \right\}^{m_x}. \quad (6.7)$$

This, with (6.5) theoretically permits us to compute the effect of the degeneracy on the virial coefficients.

Turning to the other limit—large degeneracy and small imperfections—it is found to be more convenient to use the grand partition function (4.4), and through (3.5), (3.7), and (3.13) write this in the form

$$\exp[VP(\mathbf{z})/kT]$$

$$= \int \cdots \int \sum_{\mathbf{l},\mathbf{m}} \left[\prod_{x=s,a} \frac{z_x{}^{m_x+l_x}}{m_x! l_x!} B_x\{l_x\} \right]$$

$$\times F_{\text{Class}}(\mathbf{o}, \{\mathbf{m}+\mathbf{l}\}) d\{\mathbf{m}\} d\{\mathbf{l}\}. \quad (6.8)$$

Now use the classical form of (6.1) on the right of this, neglecting, however, the cluster functions of the second kind; we obtain at once

$$\exp[VP(\mathbf{z})/kT] = \sum_{\mathbf{l}} \left[\prod_{x=s,a} \exp\{ \sum_m V b_{xm} z_x{}^m \} \right]$$

$$\times \int \cdots \int \left[\prod_{x=s,a} \frac{z_x{}^{l_x}}{l_x!} B_x{}^*\{l_x\} \right]$$

$$\times F_{\text{Class}}(\mathbf{o}, \{\mathbf{l}\}) d\{\mathbf{l}\}, \quad (6.9)$$

where b_{sm} and b_{am} are the classical irreducible integrals for the B.E. and F.D. components, respectively. The exponential factor on the right is identical with the grand partition function in the absence of degeneracy, so that the equation can be thrown into a very convenient form; namely: Let

$$\Delta P(\mathbf{z}) = P(\mathbf{z})_{\text{quant}} - P(\mathbf{z})_{\text{Class}}. \quad (6.10)$$

Then we have

$$\exp[V\Delta P(\mathbf{z})/kT] = \sum_{\mathbf{n}} \prod_{x=s,a} \frac{z_x{}^{n_x}}{n_x!} G_x(n_x), \quad (6.11)$$

where

[13] See reference 2, Eq. (57).

$$\left. \begin{aligned} G_s(n_s) &\equiv \int \cdots \int B_s{}^*\{n_s\} \\ &\qquad \times F_{\text{Class}}(o, \{n_s\}) d\{n_s\} \\ \text{and} \\ G_a(n_a) &\equiv \int \cdots \int B_a{}^*\{n_a\} \\ &\qquad \times F_{\text{Class}}(o, \{n_a\}) d\{n_a\} \end{aligned} \right\}. \quad (6.12)$$

Because of (6.10), (6.11) looks as though all the virial coefficients have been included, but in fact this is deceptive. If we had included the cluster functions of the second kind in an exact treatment, they would have appeared in a very inconvenient way in the integrands of G_s and G_a.

The integrals (6.12) can be estimated rather easily, provided the distribution functions F_{Class} behave with sufficient mildness, so that (6.11) is a very convenient theorem by means of which to compute the effect of small imperfections on the lambda-transition. It reduces to (5.1) for the perfect gas mixture.

7. MIXED LIQUIDS

In studying liquids, the second of the approximations used in imperfect gases is inapplicable because the intermolecular forces cannot be regarded as small perturbations. An entirely different approach is therefore needed to reach the lambda-transition in the liquid phase, and it can hardly be expected that the very general formulae, to be obtained can give more than a qualitative explanation. We shall start from (4.6), the modification of the generalized grand partition function; and from (2.11) write

$$F(\mathbf{z}, \{\mathbf{N}\}) = F_{\text{Class}}(\mathbf{z}, \{\mathbf{N}\}) \prod_s B_s\{N_s\} \prod_a B_a\{N_a\}.$$

In the liquid it cannot be supposed that $F_{\text{Class}}(\mathbf{z}, \{\mathbf{N}\})$ is even approximately factorizable in the components of the mixture; we therefore write this in the form

$$F(\mathbf{z}, \{\mathbf{N}\}) = F_{\text{Class}}(\mathbf{z}, \{\mathbf{N}\}) B\{\mathbf{N}\}. \quad (7.1)$$

Analogously, with (3.5) we write

$$B\{\mathbf{N}\} = \sum_{\{\mathbf{M}\}} {}_N B^*\{\mathbf{M}\}, \quad (7.2)$$

and the classical form of (6.1), namely,

$$F_{\text{Class}}(\mathbf{z}, \{\mathbf{N}\}) = \sum \{\mathbf{k}\{n_i\} \mathbf{N} - \mathbf{M}\}_u$$

$$\left[\prod_{i=1}^k \{ f_n(\{m_i\} \mathbf{N} - \mathbf{M}) + \sum_{\{m\} M} \right.$$

$$\left. \times f_{nm}(\{m\} M, \{n_i\} N - M) \} \right] F_{\text{Class}}\{\mathbf{M}\}. \quad (7.3)$$

Then,

$$\int \cdots \int F_{\text{Class}}(\mathbf{z}, \{\mathbf{N}\}) d\{\mathbf{N} - \mathbf{M}\}$$

$$= F_{\text{Class}}\{\mathbf{M}\} \left[\prod_{x=s,a} (N_x - M_x)! M_x! \right] \sum_{\mu_m}$$

$$\times \prod_m \frac{1}{\mu_m!} \{V b_n(\mathbf{z}) + \sum_{\{m\}M} b_{mn}(\mathbf{z}, \{m\}M)\}^{\mu_m}. \quad (7.4)$$

However,

$$\int \cdots \int F(\mathbf{z}, \{\mathbf{N}\}) d\{\mathbf{N}\}$$

$$= \sum_{\{\mathbf{M}\}}^{\mathbf{N}} \int \cdots \int B^*\{\mathbf{M}\} \int \cdots \int$$

$$\times F_{\text{Class}}(\mathbf{z}, \{\mathbf{N}\}) d\{\mathbf{N} - \mathbf{M}\} d\{\mathbf{M}\};$$

$$\therefore \quad \frac{1}{N!} \int \cdots \int F(\mathbf{z}, \{\mathbf{N}\}) d\{\mathbf{N}\}$$

$$= \sum_{\mathbf{n}} \prod_{s,a} \frac{1}{M_s! M_a!} \int \cdots \int B^*\{M\} F_{\text{Class}}\{\mathbf{M}\}$$

$$\times \sum_{\mu_n} \prod_n \frac{1}{\mu_n!} \{V b_n + \sum_{\{m\}M} b_{mn}(\{m\}M)\}^{\mu_n} d\{\mathbf{M}\}. \quad (7.5)$$

Because in (7.5) $\sum_n n\mu_n = N - M$, we can rewrite it in a form immediately useful in transforming (4.6); namely,

$$\sum_{\mathbf{N}} \left[\prod_{x=s,a} \frac{1}{N_x!} \left\{ \frac{y_x \rho_x(z_x)}{z_x} \right\}^{N_x} \right]$$

$$\times \int \cdots \int F(\mathbf{z}, \{\mathbf{N}\}) d\{\mathbf{N}\}$$

$$= \sum_{\mathbf{M}} \left[\prod_{x=s,a} \frac{1}{M_x!} \left\{ \frac{y_x \rho_x(z_x)}{z_x} \right\}^{M_x} \right]$$

$$\times \int \cdots \int B^*\{\mathbf{M}\} F_{\text{Class}}\{\mathbf{M}\}$$

$$\times \sum_{\mu_n} \prod_{\{n\}} \frac{1}{\mu_n!} [\{V b_n + \sum_m b_{mn}\}$$

$$\times \{y_x \rho_x(z_x)/z_x\}^n]^{\mu_n} d\{\mathbf{M}\}. \quad (7.6)$$

Unfortunately the irreducible integral b_{mn} is a function of $\{\mathbf{M}\}$ so the b-factor cannot be removed from the integral sign. In order to make further progress we shall have to assume here that it is sufficiently exact to take an average of the b-terms such that

$$\int \cdots \int B^*\{M\} F_{\text{Class}}\{\mathbf{M}\} \sum_{\mu_n} \prod_{\{n\}} \frac{1}{\mu_n!}$$

$$\times [\{V b_n + \sum_m b_{mn}\} \{y_x \rho_x(z_x)/z_x\}^n]^{\mu_n} d\{\mathbf{M}\}$$

$$= \sum_{\mu_n} \prod_n \frac{1}{\mu_n!} [V b_n^* \{y_x \rho_x(z_x)/z_x\}^{n_x}]^{\mu_n}$$

$$\times \int \cdots \int B^*\{M\} F_{\text{Class}}\{\mathbf{M}\} d\{\mathbf{M}\}, \quad (7.7)$$

where b_n^* is a suitably modified expression for b_n. Because in any case b_{mn} are small corrections compared with b_n this will be a passable approximation for a first attack upon the problem. Equations (7.6) and (7.7) now permit (6.6) to be written

$$\exp\left[VP(\mathbf{y} + \mathbf{z})/kT + \sum_{\mathbf{n}} b_n^* \left\{ \frac{y\rho(z + y)}{z + y} \right\}^n \right]$$

$$\times \sum_{\mathbf{M}} \prod_{x=s,a} \frac{1}{M_x!} \left\{ \frac{y_x \rho_x(y_x + z_x)}{y_x + z_x} \right\}^{M_x}$$

$$\times \int \cdots \int B^*\{M\} F_{\text{Class}}(\mathbf{y} + \mathbf{z}, \{\mathbf{M}\}) d\{\mathbf{M}\}$$

$$= \exp\left[VP(\mathbf{z})/kT + \sum_{\{n\}} b_n^* \left\{ \frac{y\rho(z)}{z} \right\} \right]$$

$$\times \sum_{\mathbf{M}} \prod_{x=s,a} \frac{1}{M_x!} \left\{ \frac{y_x \rho_x(z_x)}{z_x} \right\}^{M_x}$$

$$\times \int \cdots \int B^*\{\mathbf{M}\} F_{\text{Class}}(\mathbf{z}, \{\mathbf{M}\}) d\{\mathbf{M}\}. \quad (7.8)$$

For the sake of brevity we write

$$VP^*(\mathbf{z})/kT = VP(\mathbf{z})/kT + \sum_{\{n\}} b_n^* \left\{ \frac{y\rho(z)}{z} \right\}^n, \quad (7.9)$$

so that (7.7) can be written as

$$\exp[VP^*(\mathbf{y}+\mathbf{z})/kT]\sum_{\mathbf{M}}\prod_x \frac{1}{M_x!}\left\{\frac{y_x\rho_x}{y_x+z_x}\right\}^{M_x}$$

$$\times \int \cdots \int B^*\{\mathbf{M}\}F_{\text{Class}}(\mathbf{y}+\mathbf{z}, \{\mathbf{M}\})d\{\mathbf{M}\}$$

$$=\exp[VP^*(\mathbf{z})/kT]\sum_{\mathbf{M}}\prod_x \frac{1}{M_x!}\left\{\frac{y_x\rho_x}{z_x}\right\}^{M_x}$$

$$\times \int \cdots \int B^*\{M\}F_{\text{Class}}(\mathbf{z}, \{\mathbf{M}\})d\{\mathbf{M}\}. \quad (7.10)$$

Now whatever the distribution functions may be numerically, they may be regarded as modulation factors not greatly sensitive to temperature changes provided we are not near either the freezing or boiling points. Qualitatively we may then suppose that integrals of the form

$$\int \cdots \int B\{\mathbf{M}\}F_{\text{Class}}(\mathbf{z}, \{\mathbf{M}\})d\{\mathbf{M}\}$$

can be expanded in the same general way as (3.10) but with suitably modified terms I_l^* instead of I_l. Without numerical computation of an arduous nature it does not seem possible to make more than this very vague statement, and so to write down (7.10) in a form which has no more than qualitative significance, namely,

$$\exp\left[VP^*(\mathbf{y}+\mathbf{z})/kT+\sum_{x=s,a}\sum_{l \geqslant 1}\right.$$

$$\left. \times VI_{xl}^*(-1)^{(l-1)\delta_{xa}}\left\{\frac{y_x\rho_x(\mathbf{y}+\mathbf{z})}{y_x+z_x}\right\}^l\right]$$

$$=\exp\left[VP^*(\mathbf{z})/kT+\sum_{x=s,a}\sum_{l \leqslant 1}\right.$$

$$\left. \times VI_{xl}^*(-1)^{(l-1)\delta_{xa}}\left\{\frac{y_x\rho_x(\mathbf{z})}{z_x}\right\}^l\right], \quad (7.11)$$

or

$$P^*(\mathbf{y}+\mathbf{z})-P^*(\mathbf{z})=kT\sum_{x=s,a}\sum_{l \geqslant 1}I_{xl}^*(-1)^{(l-1)\delta_{xa}}$$

$$\times y_x^l\left[\left\{\frac{\rho_x(\mathbf{y}+\mathbf{z})}{y_x+z_x}\right\}^l-\left\{\frac{\rho_x(\mathbf{z})}{z_x}\right\}^l\right]. \quad (7.12)$$

The behavior of such a liquid near the lambda-point is controlled by the convergence characteristics of the series $\sum_l I_{sl}^* y_s{}^l$ the transition temperature being such that y_s has a value coinciding with the radius of convergence of the series. Although we know nothing about the numerical values of I_{sl}^* we can assert that they will depend upon l in a manner essentially the same as I_{sl} for the gas, namely,

$$I_{sl} \backsim \chi^{l-1}/l^\nu,$$

where χ is some function of T increasing with decreasing T, and ν some nearly constant number. The radius of convergence would, under these circumstances, exist; namely $y_{s\lambda}=1/\chi(T_\lambda)$.

The only conclusions that can be drawn from the foregoing argument are:

(a) The Bose-Einstein lambda-transition does in general exist even if the assembly is in a liquid phase, at the temperature.

(b) In a mixture of liquids it is only very roughly true to say that the Bose-Einstein degeneracies are additive; although the component with the highest lambda-transition temperature may be expected to be responsible for the B.E. condensation of the mixture. What happens below this transition is entirely beyond the scope of the theory.

8. SOLUTIONS AND LIQUID MIXTURES OF ISOTOPES

The formula (6.7) developed for the effect of quantum degeneracy on the imperfect gas is still applicable for the liquid phase, provided the fugacity set $\{z\}$ is given the appropriate value. Consider first the general case in which several solutes are present in a solvent, and to simplify the notation regard the latter as a pure liquid of one component of unspecified statistics. Following McMillan and Mayer[2] (l.c.) we take as standard state that with zero solute activity, so that the fugacity set $\{\mathbf{y}\}$ represents total effect of the solutes present. The pressure difference given by (6.7) is then just the osmotic pressure P_0 of the solutes, and we may write that equation as

$$P_0(\mathbf{z}, \mathbf{y})=kT\sum_{\mathbf{m}}b_m^*(\mathbf{z})\prod_s a_s{}^{m_s}\prod_a a_a{}^{m_a}, \quad (8.1)$$

where a_s represents the activity $y_s\rho_s(z)/z$ of the s-component solute. Alternatively,

$$P_0(\mathbf{z}, \mathbf{a})=kT[\sum_s a_s+\sum_a a_a$$

$$+\sum_{\mathbf{m} \geqslant 2}b_m^*(\mathbf{z})\prod_{s,a}a_s{}^{m_s}a_a{}^{m_a}]. \quad (8.2)$$

All terms in $b_m{}^*$ in which **m** contains solvent particles disappear from the expression because the y-factor is zero for such terms if the solvent is supposed to maintain its standard fugacity. In general, $b_m{}^*$ depends upon how many particles of the various components are present in the set **m**, but for mixtures of isotopes the only distinction that has to be made is that between the B.E. and F.D. types. If in particular we have a single B.E. isotopic component dissolved in an F.D. solvent, we may write (8.2) in the very simple form

$$P_0(z, a_s) = kT[a_s + \sum_{m \geqslant 2} b^*(z, m)a_s{}^m], \quad (8.3)$$

where from (6.5)

$$Vm!b^*(m) \equiv \int \cdots \int \sum \{k\{n_i\}m\}_u$$

$$\times \prod_{i=1}^{k} g_s(\{n_i\}m)f_m(z, \{m\})d\{m\}, \quad (8.4)$$

f_m being the classical cluster functions. Similarly for an F.D. solute in a B.E. solvent

$$P_0(z, a_a) = kT[a_0 + \sum_{m \geqslant 2} b^*(z, m)a_a{}^m], \quad (8.5)$$

with

$$Vm!b^*(z, m) \equiv \int \cdots \int \sum \{k\{n_i\}m\}_u$$

$$\prod_{i=1}^{k}(-1)^{(n_i-1)}g_a(\{n_i\}m)f_m(z, \{m\})d\{m\}. \quad (8.6)$$

These results enable us to estimate the effect of quantum degeneracy on the osmotic pressure of solutes of either type, and we note that the results are practically independent of any quantum degeneracy in the solvent. This is especially interesting in the case of He_3 in He_4, and it means that we can apply the usual laws of partial pressures to the He_3 component in liquid helium at all temperatures down to the lambda-point.

The writer wishes to thank Professor Joseph E. Mayer for many stimulating discussions.