SOVIET PHYSICS JETP VOLUME 29, NUMBER 4 OCTOBER, 1969

EQUATION OF STATE OF AN EXCITED GAS

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Submitted October 29, 1968

Zh. Eksp. Teor. Fiz. 56, 1325–1337 (April, 1969)

The virial equation of state of an excited gas consisting of atoms of a given chemical element, part of the atoms of which are excited to a given energy level, is derived by the quantum group expansion technique. The number of excited atoms may be arbitrary and hence the electron distribution over the atomic levels is nonequilibrium. It is assumed, however, that thermal equilibrium of translational motion of the gas atoms is established in the system. A formula for estimating the third virial coefficient of a resonance-excited gas is derived and is valid at room temperatures. The role of three-particle collisions in a resonance-excited gas is discussed. The second virial coefficient of metastable excited atoms of a gas, in which quadrupole-quadrupole interaction between the excited atoms is significant, is estimated.

WE investigate in this paper the equation of state of a gas consisting of N_0 atoms of the same chemical element. Let N' atoms be excited to the electronic level ϵ', and the remaining $N = N_0 - N'$ atoms be in the ground state with an electron energy equal to ϵ. (We shall assume henceforth that the number of excited atoms N' is specified arbitrarily.)

The question of applying equilibrium statistics to such a system was discussed in[1]. It was shown there that at fixed numbers of atoms N and N', whose ratio has nothing in common with equilibrium statistics, it is possible to calculate for not too rarefied gases the partition function with respect to the translational degrees of freedom. The point is that the time of establishment of equilibrium with respect to the translational motion is much shorter than the time required to change the electron energy. Therefore, equilibrium over the translational degrees of freedom can be established while the distribution of the electrons over the atomic levels is not in equilibrium. This equilibrium may even be stationary in time, if the numbers N and N' are kept constant by external means. An example of such an action may be the pumping light in a gas laser, which maintains a definite number of molecules at a specified energy level.

If dipole transitions are allowed between the states ϵ and ϵ' then a resonant dipole-dipole interaction (henceforth abbreviated D-D) is produced between the atom in the ground state and the atom in the excited state. As is well known, the energy of this interaction differs from zero in the first perturbation-theory approximation, and is inversely proportional to r^3 (r—distance between the atoms).

It turns out that the contribution of the resonant D-D interaction between the differently excited atoms to the thermodynamic functions greatly exceeds the corresponding contribution from the usual Van der Waals interaction. In particular, it leads to an anomalously large second virial coefficient. There are therefore large deviations from ideal behavior in the system under consideration even at relatively small contents of the excited atoms[1]. These results were obtained neglecting the interaction between equally-excited atoms.

We note that allowance for the latter may be of certain interest. Cases are possible when this interaction is decisive. Indeed, let the ground state ϵ be an S state, and let the state ϵ' have nonzero orbital and total angular momenta. Assume further that the dipole transitions from the state ϵ' to the state ϵ are forbidden. In this case the energy of interaction between atoms in the ground state as well as between differently-excited atoms, differs from zero only in the second perturbation-theory approximation, whereas the quadrupole-quadrupole (henceforth Q-Q) interaction of the excited atoms differs from zero already in the first perturbation-theory approximation. This interaction can be either attractive or repulsive, depending on the set of "molecular quantum" numbers characterizing the pair of colliding atoms, and decreases with distance like $1/r^5$ [2]. London[3] was the first to investigate Q-Q interactions. Subsequently Knipp[4] calculated the energy of the Q-Q interaction of a whole series of pairs of atoms, the ground state of which is not an S state. It turns out that the energy of the Q-Q interaction of the excited atoms is much larger than the dispersion energy, i.e., than the Van der Waals energy[5], and consequently, at sufficient concentrations of excited metastable atoms, it can greatly influence the thermodynamic functions of the system.

It is noted in the literature that the Q-Q interaction, like the resonant D-D interaction, makes no contribution to the thermodynamic functions of the gas when averaged over all the possible states of their system (at specified states of the atoms), including all the possible orientations of the angular momenta of the atom. This statement is valid at high temperatures, when the correlation of the virtual multipoles can be neglected. If the energy of the Q-Q interaction is of the order of and larger than kT, then, like the resonant D-D interaction, the Q-Q interaction will give a nonzero contribution to the thermodynamic functions.

By virtue of the foregoing, it is advisable to obtain an equation of state that takes into account the interaction between equally excited atoms.

1. VIRIAL EQUATION OF STATE OF AN EXCITED GAS

The partition function of the gas under consideration, at fixed numbers of atoms N and N′, can be represented in the form[1]

$$Z = \mathrm{Sp}\, e^{-\beta H} = Z_0 \int dR \sum_s e^{-\beta E_s(R)};$$

$$Z_0 = \left(\frac{M}{2\pi\hbar^2\beta}\right)^{3N_0/2}; \quad \beta \equiv \frac{1}{kT}, \tag{1.1}$$

H is the energy operator of the entire gas; Z_0 is the result of calculating the trace over the translational motion, which we assume to be quasiclassical (the system is in thermodynamic equilibrium with respect to the translational motion); M is the mass of the atom; $E_s(R)$ is the energy of the electron motion of all the atoms of the gas, calculated in the adiabatic approximation (the fast subsystem is the electron system), $R(\ldots R_j \ldots)$ is the set of coordinates of the centers of gravity of the atoms of the entire gas, R_j is the three-dimensional vector of the center of gravity of the j-th atom; s is the aggregate of the quantum numbers of the electron motion, corresponding to the states of the system with fixed numbers N and N′ (we recall that there is no thermal equilibrium with respect to the electronic degrees of freedom—the number of atoms with energies ϵ' is set arbitrarily).

It will be convenient to put $E_s(R) = E_0 + W_s(R)$, where $E_0 = \epsilon N + \epsilon' N'$ is the energy of the non-interacting atoms, and $W_s(R)$ is the energy of their interaction. It is obvious that $W_s(R) \to 0$ as $|R_i - R_j| \to \infty$ for all pairs of atoms simultaneously.

To obtain virial expansions of the thermodynamic functions of the excited gas, we shall use a device proposed by Kahn and Uhlenbeck[6] known as the "method of group quantum expansions" (henceforth GQE). The difference between the method employed below to find the equation of state and the traditional GQE method (see, for example[7]) lies in the fact that we assume $W_s(R)$ to be known, for example, from perturbation theory.

We apply the GQE method to the representation $\sum_s \exp(-\beta W_s R)$ in the form of a combination of group functions. We denote by $s_{ll'}$ the aggregate of quantum numbers of the group of particles that have come close together, in which l atoms have an electron energy ϵ, and l' atoms have an electron energy ϵ' (l' is the number of excited atoms or the number of excitations); $W_{ll'}(1, \ldots, l + l')$ is the interaction energy of a group of $l + l'$ atoms, on which l' excitations are localized (one excitation per particle); 1, 2, ... $l + l'$ denote in abbreviated form the coordinates of the centers of gravity of the considered group of atoms.

To determine the sequence of the group functions $u_{ll'}(1, 2, \ldots, l + l')$, we shall follow[7]. We introduce the symbol

$$\mathscr{E}_{s_{ij}}(1, 2, \ldots) = \exp\{-\beta W_{s_{ij}}(1, 2, \ldots)\}.$$

For one isolated particle we have

$$\sum_{s_{10}} \mathscr{E}_{s_{10}}(1) = \sum_{s_{10}} 1 = g = u_{10}(1)$$

or

$$\sum_{s_{01}} \mathscr{E}_{s_{01}}(1) = \sum_{s_{01}} 1 = g' = u_{01}(1) \tag{1.2}$$

depending on the electron energy possessed by the atom, g and g′ are the multiplicities of the degeneracy of the levels of ϵ and ϵ', respectively.

Let us determine the two-particle group functions. For a pair of particles the following cases are possible:

a) both atoms have electron energies ϵ, and then

$$\sum_{s_{20}} \mathscr{E}_{s_{20}}(1,2) = u_{10}(1)u_{10}(2) + u_{20}(1,2),$$

whence we get with allowance for (1.2)

$$u_{20}(1,2) = \sum_{s_{20}} [\mathscr{E}_{s_{20}}(1,2) - 1]; \tag{1.3}$$

b) both atoms have an electron energy ϵ':

$$\sum_{s_{02}} \mathscr{E}_{s_{02}}(1,2) = u_{01}(1)u_{01}(2) + u_{02}(1,2),$$

whence

$$u_{02}(1,2) = \sum_{s_{02}} [\mathscr{E}_{s_{02}}(1,2) - 1]; \tag{1.4}$$

c) one of the particles has an electron energy ϵ and the other ϵ':

$$\sum_{s_{11}} \mathscr{E}_{s_{11}}(1,2) = u_{10}(1)u_{01}(2) + u_{01}(1)u_{10}(2) + u_{11}(1,2). \tag{1.5}$$

The presence of the first two terms in (1.5) is connected with the fact that when $|R_1 - R_2| \to \infty$ the excitation is localized on one of the particles. From (1.5) with allowance for (1.2) we obtain

$$u_{11}(1,2) = \sum_{s_{11}} [\mathscr{E}_{s_{11}}(1,2) - 1]. \tag{1.6}$$

It is obvious that when $|R_1 - R_2| \to \infty$ we have u_{20}, u_{02}, $u_{11} \to 0$.

The determination of the group functions of brought together equally excited particles does not differ in any way from the corresponding method of[7]. In the determination of the group functions of brought-together differently-excited particles, it must be taken into account that the excitations migrate in exciton fashion over the atoms of the group, and therefore it is impossible to point out the particular atoms from the group that are excited. For example, for a group of three brought-together particles, of which one is excited, we get

$$\sum_{s_{21}} \mathscr{E}_{s_{21}}(1,2,3) = \sum [u_{10}(1)u_{10}(2)u_{01}(3) + u_{10}(1)u_{11}(2,3) + u_{01}(1)u_{20}(2,3)] + u_{21}(1,2,3), \tag{1.7}$$

with summation over the cyclic permutations of the arguments of the functions $u_{ll'}$ in the right side of (1.7). From (1.7), with allowance for (1.2), (1.3), and (1.6), we obtain

$$u_{21}(1,2,3) = \sum_{s_{21}} [\mathscr{E}_{s_{21}}(1,2,3) - 1] - g \sum_{j>i=1}^{3} \sum_{s_{11}} [\mathscr{E}_{s_{11}}(i,j) - 1] - g' \sum_{j>i=1}^{3} \sum_{s_{20}} [\mathscr{E}_{s_{20}}(i,j) - 1] \tag{1.7a}$$

and analogously for a group of three particles with two excitations

$$u_{12}(1,2,3) = \sum_{s_{12}} [\mathscr{E}_{s_{12}}(1,2,3) - 1] - g' \sum_{j>i=1} \sum_{s_{11}} [\mathscr{E}_{s_{11}}(i,j) - 1]$$

$$-g\sum_{j>i=1}\sum_{s_{02}}[\mathscr{E}_{s_{02}}(i,j)-1]. \tag{1.7b}$$

If the foregoing reasoning is continued and the number of particles and excitations in the group is gradually increased, we obtain for a system of N_0 particles with N′ excitations finally,

$$\sum_{s}\exp\{-\beta W_s(R)\}=\sum_{\{m_{ll'}\}}\sum_{p}[u_{10}(\ )u_{10}(\ )\ldots][u_{01}(\ )u_{01}(\ )\ldots]$$
$$\times[u_{20}(,\ )u_{20}(,\ )\ldots][u_{11}(,\ )u_{11}(,\ )\ldots]\ldots[u_{ll'}(,,\ldots)\ldots]\ldots. \tag{1.8}$$

We incidentally determine thereby all the group functions $u_{ll'}$ (1, 2, ..., $l + l'$). Here $m_{ll'}$ is zero or a positive integer, and the choice of the numbers $\{m_{ll'}\}$ should satisfy the conditions

$$\sum_{l=1}^{N}\sum_{l'=0}^{N'}lm_{ll'}=N,\qquad \sum_{l=0}^{N}\sum_{l'=1}^{N'}l'm_{ll'}=N'. \tag{1.8a}$$

$\sum_p$ in (1.8) is the sum over all different methods of filling the empty places in the arguments of the functions $u_{ll'}$ (,,...) by the coordinates $R_1, R_2, \ldots, R_{N_0}$.

We introduce the group integrals

$$b_{ll'}=\frac{1}{(l+l')!\,g^l g'^{l'}V}\int d^3R_1\ldots d^3R_{l+l'}\,u_{ll'}(1,\ldots,l+l'), \tag{1.9}$$

where V is the volume in which the gas is situated. Substituting (1.8) in (1.1) and taking into account (1.9), (1.8a) and the symmetry of $u_{ll'}$ against permutations of the arguments, we sum over p, after first interchanging $\sum_p$ and $\int dR$, and after cancelling out $N_0!$ (which is equivalent to taking into account the identity of the particles) we obtain in analogy with[7]

$$Z=Z_0 g^N g'^{N'}e^{-\beta E_0}\sum_{\{m_{ll'}\}}\prod_{l}^{N}\prod_{l'}^{N'}\frac{1}{m_{ll'}!}(Vb_{ll'})^{m_{ll'}}. \tag{1.10}$$

We now proceed to calculate formula (1.10) under the conditions (1.8a). A similar problem was solved by Born and Fuchs to determine the virial equation of the state of a single-component unexcited gas[8]. We introduce the generating function

$$\lambda(z,z')=\exp\left\{\sum_{l}^{N}\sum_{l'}^{N'}Vb_{ll'}z^l z'^{l'}\right\}, \tag{1.11}$$

where z and z′ are complex variables; l and l' do not vanish simultaneously. The coefficient $z^N z'^{N'}$ in the expansion of λ(z, z′) in powers of z and z′ coincides with

$$Q_{NN'}=\sum_{\{m_{ll'}\}}\prod_{l}^{N}\prod_{l'}^{N'}\frac{1}{m_{ll'}!}(Vb_{ll'})^{m_{ll'}}.$$

According to the Cauchy theorem for functions of complex variables we have

$$Q_{NN'}=\frac{1}{(2\pi i)^2}\oint dz'\oint dz\frac{\lambda(z,z')}{z^{N+1}z'^{N'+1}}. \tag{1.12}$$

The integration contours in (1.12) should encircle the points z = 0 and z′ = 0 in the corresponding complex planes, and can be arbitrary in all other respects. We shall calculate the integral (1.12) by the saddle-point method for two variables. The saddle-points are determined from the solution of the system of equations

$$\frac{\partial}{\partial z}f(z,z')=0,\qquad \frac{\partial}{\partial z'}f(z,z')=0, \tag{1.13}$$

where

$$f(z,z')=\ln\lambda(z,z')-(N+1)\ln z-(N'+1)\ln z'.$$

We introduce the particle densities n = N/V and n′ = N′/V. Recognizing that N, N′ ≫ 1, we transform (1.13) into

$$\sum_{l=1}^{N}\sum_{l'=0}^{N'}lb_{ll'}z^l z'^{l'}=n;\qquad \sum_{l=0}^{N}\sum_{l'=1}^{N'}l'b_{ll'}z^l z'^{l'}=n'. \tag{1.13a}$$

After integrating (1.12) we get

$$Z\approx Z_0 e^{-\beta E_0}\frac{g^N g'^{N'}}{2\pi}\sum_{i}\exp\{f(\xi_i\xi_i')\}/\sqrt{\Delta(\xi_i\xi_i')}, \tag{1.14}$$

ξ_i and ξ_i' are the saddle points, which make a comparable contribution to the partition function (1.14),

$$\Delta(\xi_i,\xi_i')=\frac{\partial^2 f}{\partial\xi_i^2}\frac{\partial^2 f}{\partial\xi_i'^2}-\frac{\partial^2 f}{\partial\xi_i\,\partial\xi_i'}$$

For the case of small densities n and n′, the system (1.13a) has a unique real solution z = ξ, z′ = ξ′. Expressions for ξ and ξ′ can be obtained in the form of series in powers of the densities n and n′.

We obtain the equation of state by eliminating ξ and ξ′ from

$$p=kT\left(\frac{\partial\ln Z}{\partial V}\right)_T=kT\sum_{ll'}b_{ll'}\xi^l\xi'^{l'} \tag{1.15}$$

with the aid of the system (1.13a). Relation (1.15) is obtained from (1.14) by neglecting ln Δ, which is permissible, since the argument of the exponential in (1.14) is f(ξ, ξ′) ~ NN′, and Δ ~ $(NN')^2$. Thus, formula (1.15) together with the solutions of the system (1.13) makes it possible to obtain an equation of state in the form of a series in powers of the densities n and n′, and the coefficients of the series are expressed in terms of the group integrals (1.9).

Accurate to terms of third order in the density, the equation of state is

$$p=kT[n+n'-n^2b_{20}-nn'b_{11}-n'^2b_{02}+n^3(4b_{20}^2-2b_{30})$$
$$+n^2n'(b_{11}^2+4b_{20}b_{11}-2b_{21})+nn'^2(b_{11}^2+4b_{02}b_{11}-2b_{12})$$
$$+n'^3(4b_{02}^2-2b_{03}^2)+\ldots]. \tag{1.16}$$

We note that when n′ = 0 Eq. (1.16) goes over into the virial equation of state of a real gas, in which the virial coefficients are expressed in terms of the group integrals[5,7]. The coefficient of nn′ coincides with the expression obtained in[1] by another method.

Let us proceed to discuss the equation of state in limiting cases of a resonantly excited gas and a gas of metastable excited atoms.

2. RESONANTLY EXCITED GAS

Assume that optical dipole transitions are allowed between the ground state of the atom ϵ and the excited state ϵ′; then, as already indicated, the main contribution to the equation of state is made by the resonant D-D interaction between differently excited atoms. Neglecting the interaction of equally excited atoms, we obtain on the basis of (1.16) an equation of state with allowance for three-particle interactions:

$$p=kT[n+n'-b_{11}nn'+(b_{11}^2-2b_{21})n^2n'+(b_{11}^2-2b_{12})nn'^2]. \tag{2.1}$$

To calculate the third virial coefficient it is sufficient to find the group integrals b_{21} and b_{12}, which describe the group of three atoms with one and two excitations respectively, since the group integral b_{11} was considered in[1]. The group integrals b_{21} and b_{12} can be obtained from formulas (1.7a), (1.7b), and (1.9):

$$b_{21} = \frac{1}{3!Vg^2g'}\int d^3R_1d^3R_2d^3R_3\left\{\sum_{s_{21}}[\mathscr{E}_{s_{21}}(1,2,3)-1] - g\sum_{j>i=1}\sum_{s_{11}}[\mathscr{E}_{s_{11}}(i,j)-1]\right\}, \tag{2.2}$$

$$b_{12} = \frac{1}{3!Vgg'^2}\int d^3R_1d^3R_2d^3R_3\left\{\sum_{s_{12}}[\mathscr{E}_{s_{12}}(1,2,3)-1] - g'\sum_{j>i=1}\sum_{s_{11}}[\mathscr{E}_{s_{11}}(i,j)-1]\right\}. \tag{2.2a}$$

As seen from (2.1) and (2.2), the first stage in the calculation of b_{21} is to find the energy of interaction of the group of three atoms with one excitation, $W_{S_{21}}$. A similar problem of calculating the interaction energy of n identical atoms, on which one excitation is localized, was considered by Frenkel'[9] in an attempt to determine the influence of resonant D-D interaction on the shape of a spectral line. The same process was discussed by Weisskopf[10]. As a result certain general properties of the roots of the secular perturbation-theory equation were obtained, from which it is necessary to determine the interaction energy of a group of n atoms, on which one excitation is localized (see also the review[11]). In the calculation of $W_{S_{21}}$ it is necessary to take into account the degeneracy connected with the exchange of excitations between the atoms, and the degeneracy with respect to the projections of the orbital angular momentum. The latter complicates the problem to a considerable degree.

The calculation of $W_{S_{21}}$ for a gas of resonantly-excited atoms situated in a strong magnetic field was performed by Vdovin[12]. If the magnetic field is so strong that the energy differences of the Zeeman sublevels greatly exceed the splitting due to the resonant D-D interaction, then the calculation of the interaction energy of two unexcited and one excited atom is greatly simplified. The point is that in this case the degeneracy with respect to the projections of the orbital angular momenta of the atoms is lifted, and all that remains is the degeneracy connected with the exchange of excitations between the atoms. The group integral b_{21} for such a gas was first considered in[12]. We undertake below an attempt to take into account the degeneracy in the projections of the orbital angular momentum in the calculation of b_{21}.

We now proceed to determine $W_{S_{21}}$, $W_{S_{12}}$, and $W_{S_{11}}$. We consider first $W_{S_{21}}$. We carry out the calculation by the perturbation-theory method for a concrete case. Assume that an atom with electron energy ϵ is in the ground state $^1S_0$ and is described by a wave function φ_0. The excited atom with electron energy ϵ' is in the state $^1P_1$ and is described by three wave functions ψ_1, ψ_0, and ψ_{-1}, which are numbered in accordance with the values of the magnetic quantum number. We neglect the fine structure, and then we get in our case g = 1, and g′ = 3. We choose the coordinate axes in the following manner: the z axis is perpendicular to the plane in which the group of three atoms is located, and the arrangement of the x and y axes is shown in Fig. 1. In the zeroth perturbation-theory approximation, the system of three atoms with one excitation has an energy equal to $2\epsilon + \epsilon'$. In our coordinate system, this energy corresponds to nine degenerate functions of the type

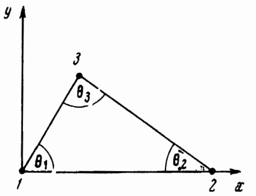

FIG. 1. Coordinate system. The numbered points denote the positions of the atoms.

$$\Psi_1 = \psi_1(r_1)\varphi_0(r_2)\varphi_0(r_3),$$
$$\Psi_2 = \psi_0(r_1)\varphi_0(r_2)\varphi_0(r_3), \qquad \Psi_3 = \psi_{-1}(r_1)\varphi_0(r_2)\varphi_0(r_3). \tag{2.3}$$

The remaining six functions are obtained from (2.3) by cyclic permutation of the arguments r_1, r_2, and r_3, where r_i is the aggregate of the coordinates of the electrons of the i-th atom. These wave functions are constructed with allowance for the possible exchange of excitation between the atoms. The interaction-energy operator of the three atoms has in the D-D approximation the form

$$W = \sum_{j>i=1}^{3}[\mathbf{p}_i\mathbf{p}_j - 3(\mathbf{p}_i\mathbf{n}_{ij})(\mathbf{p}_j\mathbf{n}_{ij})]/R_{ij}^3 \tag{2.4}$$

$\mathbf{p}_i$ is the dipole-moment vector of the i-th atom, $\mathbf{n}_{ij}$ is a unit vector in the direction from the i-th atom to the j-th atom, R_{ij} is the distance between the i-th and j-th atoms, with $\mathbf{R}_{12} + \mathbf{R}_{23} + \mathbf{R}_{31} = 0$. We introduce $p_+ = p_x + ip_y$ and $p_- = p_x - ip_y$; we can then represent (2.4) in the form

$$W = \sum_{j>k=1}^{3}\left[p_{kz}p_{jz} - \frac{1}{4}(p_k^+p_j^- + p_k^-p_j^+) - \frac{3}{4}(p_k^+p_j^+e^{-2i\theta_{kj}} + p_k^-p_j^-e^{2i\theta_{kj}})\right]\Big/R_{kj}^3. \tag{2.5}$$

Here $\theta_{12} = 0$, $\theta_{13} = \theta_1$, and $\theta_{23} = -\theta_2$. The angles θ_1 and θ_2 are shown in Fig. 1. Formula (2.5) is valid when $0 \le \theta_1 \le \pi/2$ and $0 \le \theta_2 \le \pi/2$. We shall show later that contributions to the group integral b_{21} are made only by three-atom configurations in which θ_1 and θ_2 vary in the indicated ranges (see the Appendix). In the zeroth perturbation-theory approximation, we obtain the interaction energy $W_{S_{21}}$ by setting a ninth-order determinant equal to zero. We obtain this determinant by taking the matrix elements (2.5) on the wave functions (2.3). This determinant breaks up into a product of two determinants of third and sixth orders. After expanding these determinants, we arrive at the following equations for the determination of $W_{S_{21}}$:

$$W^3 - \tau W - 2q = 0, \tag{2.6}$$

$$W^6 + aW^4 + bW^3 + cW^2 + dW + f = 0. \tag{2.7}$$

Here

$$W \equiv W_{s_{21}},\ a = -5\tau,\ \tau = A^2[R_{12}^{-6} + R_{13}^{-6} + R_{23}^{-6}],$$

A is the square of the modulus of the matrix element of the transition between the states m = ±1, m = 0,

$$b = q(1+9\alpha)/2, \quad q = (A/R_{12}R_{13}R_{23})^3,\ \alpha = \cos 2\theta_1 + \cos 2\theta_2 + \cos 2\theta_3,$$
$$c = 4\tau^2 + 9(R_{23}^6\sin^2\theta_1 + R_{13}^6\sin^2\theta_2 + R_{12}^6\sin^2\theta_3)(q/A)^2,$$

$$d = q[(19-9\alpha)\tau - 36A^2(R_{23}^{-6}\sin^2\theta_1 + R_{13}^{-6}\sin^2\theta_2 + R_{12}^{-6}\sin^2\theta_3)],$$

$$f = q^2\left\{-1267 + 162\left[\alpha + \frac{1}{2}\sum_{i=1}^{3}\cos 4\theta_i - \sum_{j>i=1}^{3}\cos 2(\theta_i - \theta_j)\right]\right\} \Big/ 32,$$

$$\theta_3 = \pi - \theta_1 - \theta_2.$$

We note that the angles θ_1 and θ_2 can be expressed in terms of the distances R_{12}, R_{13}, and R_{23}.

Equation (2.7) simplifies greatly if all three atoms lie on a single straight line. In this case $\theta_1 = \theta_2 = 0$ and (2.7) breaks up into two equations of third degree in $W_{S_{21}}$. The first of them coincides with (2.6), and the second is given by

$$W^3 - 4\tau W + 16q = 0. \tag{2.7a}$$

For the indicated configuration, the $W_{S_{21}}$ can be obtained in analytic form

$$\begin{gathered}
W_1 = W_2 = 2\left(\frac{\tau}{3}\right)^{1/2}\cos\frac{\varphi}{3}, \quad W_3 = W_4 = -2\left(\frac{\tau}{3}\right)^{1/2}\cos\frac{\pi-\varphi}{3}, \\
W_5 = W_6 = -2\left(\frac{\tau}{3}\right)^{1/2}\cos\frac{\pi+\varphi}{3} \quad W_7 = -4\left(\frac{\tau}{3}\right)^{1/2}\cos\frac{\varphi}{3} \\
W_8 = 4\left(\frac{\tau}{3}\right)^{1/2}\cos\frac{\pi-\varphi}{3}, \quad W_9 = 4\left(\frac{\tau}{3}\right)^{1/2}\cos\frac{\pi+\varphi}{3} \\
\cos\varphi = \left(\frac{3}{\tau}\right)^{3/2} q.
\end{gathered} \tag{2.8}$$

The interaction energy $W_{S_{11}}$ of a pair of differently-excited atoms is obtained from (2.8) by taking the limit—removing one of the three particles to infinity:

$$\begin{gathered}
W_1 = W_2 = A / R_{ij}^3, \quad W_3 = W_4 = -A / R_{ij}^3, \\
W_7 = -2A / R_{ij}^3, \quad W_8 = 2A / R_{ij}^3,
\end{gathered} \tag{2.8a}$$

where $1 \leq i < j \leq 3$. In this case the "superfluous" roots $W_5 = W_6 = W_9 = 0$ which result from the fact that the number of states of the three particles with one excitation is larger than the number of states of a pair of particles with one excitation, make no contribution to b_{21}.

We were unable to obtain $W_{S_{21}}$ in analytic form for an arbitrary configuration of the three atoms. Apparently they can be obtained only approximately by numerical methods. The results of such calculations of the root W_S, corresponding to a maximum binding energy at fixed $R_{13} = R_{23}$ as a function of θ_1, reveal a relatively weak monotonic decrease of $|W_S|$ with increasing θ_1. For example, when $\theta_1 = 0$ (linear chain configuration) we have $W_S = -2.96\ A/R_{13}^3kT$. When $\theta_1 = \pi/3$ (equilateral configuration triangle) we have $W_S = -2.5\ A/R_{13}^3kT$. The slight deviation from the configuration of an isosceles triangle causes the binding energy of the three particles to go over rapidly into the binding energy of the pair of nearest particles. Thus, the greatest binding energy is possessed by a linear chain of three atoms, thus confirming the corresponding assumption[12].

From the form of Eqs. (2.6) and (2.7) it follows that the resonant D-D interaction is non-additive, and also that

$$\sum_{s=1}^{9} W_s(1,2,3) = 0$$

(s is the number of the root of the secular equation). The latter conclusions agree with the results of[9] and remain in force for a gas of excited atoms in a magnetic field[12].

We now consider a group of three particles, of which two particles have energy ϵ' and one particle has the electron energy ϵ. In the zeroth approximation, the system of three atoms has an energy $\epsilon + 2\epsilon'$, and this energy corresponds to 27 wave functions, which are constructed in analogy with the functions (2.3). It can be shown that $W_{S_{12}}$ are determined from (2.6) and (2.7), but the multiplicity of each root must be tripled. Taking the foregoing into account, and also the fact that $g = 1$ and $g' = 3$, we arrive at

$$b_{21} = b_{12}. \tag{2.9}$$

It is obvious that (2.9) is valid only if the interaction between equally excited atoms is neglected.

Equations (2.6) and (2.7) were obtained with the aid of perturbation theory. They cease to be valid at interatomic distances of the order of double the atomic radius r_0 or less. As in[1], we shall simulate the interaction potential of the atoms $W_{S_{21}}$ at distances smaller than r_0 in the following manner: $W_{S_{21}} = \infty$ if at least one of the distances $R_{ij} < r_0$; when $R_{ij} > r_0$ for all pairs of atoms simultaneously, the $W_{S_{21}}$ can be obtained from (2.6) and (2.7a). Analogous arguments hold for the potential $W_{S_{11}}$.

We proceed now to consider the group integral b_{21} of two unexcited atoms and one excited atom. Since $W_{S_{21}}$ cannot be calculated analytically for an arbitrary configuration of a group of three atoms, we can only approximately estimate b_{21}. It turns out that at room temperatures, for typical A and for $r_0 \approx 2$ Å, we have $a = A/r_0^3kT \sim 10$[1]. This enables us to obtain for b_{21} an approximate formula for the case when $a \gg 1$ (see the Appendix):

$$b_{21} \approx \frac{4\pi^2 r_0^6}{3}\left(\frac{r_0^3kT}{2.96A}\right)^{5/2}\exp\{3A/r_0^3kT\}. \tag{2.10}$$

Comparison of (2.10) with the corresponding formula of[12] shows that in the argument of the exponential the factor preceding A is $2\sqrt{2}$ in lieu of 3, and the factor preceding the exponent has a different degree of temperature dependence.

We introduce the content of the excited gas $x = N'/N_0$ and, taking (2.9) into account, we rewrite the virial equation of state in the form

$$p = N_0kT\left[1 + \frac{B(T)}{V} + \frac{C(T)}{V^2}\right], \tag{2.11}$$

$B(T) = -x(1-x)N_0b_{11}$ is the second virial coefficient, $C(T) = x(1-x)(N_0b_{11})^2\kappa$ is the third virial coefficient, and

$$\kappa = 1 - \frac{2b_{21}}{b_{11}^2} \approx 1 - 43\left(\frac{A}{r_0^3kT}\right)^{1/2}\exp\left\{-\frac{A}{r_0^3kT}\right\}.$$

In the derivation of κ we used the expression for b_{11} when $a \gg 1$[1]:

$$b_{11} \approx \frac{\pi}{9}r_0^3\left(\frac{r_0^3kT}{A}\right)\exp\left\{\frac{2A}{r_0^3kT}\right\}.$$

It is easy to see that when $a \gg 1$ the following inequality holds

$$b_{11}^2 \gg b_{21}, \tag{2.12}$$

and causes the third virial coefficient to be determined principally by the group integral of the pair collisions. The inequality (2.12) is valid also for an excited gas in a magnetic field[12]. It is indicated in the same reference that a similar situation holds also for collisions of larger multiplicity (4 and above). This makes it possible to obtain the equation of state of a resonantly-excited gas in the form

$$p = kT\{n + n' + [\sqrt{(1 + b_{11}n + b_{11}n')^2 - 4b_{11}{}^2nn'} - 1] / b_{11}\} / 2, \quad (2.13)$$

which is valid, in Vdovin's opinion[12], at densities when $b_{11}n \gtrsim 1$ and $b_{11}n' \gtrsim 1$, while the contribution of the multiparticle collisions can still be neglected. On the basis of (2.13), Vdovin states that the system under consideration is stable against decay into phases for all contents of the excited gas. It is possible that the equation of state (2.13) holds for a magnetized gas. In the absence of a field, an analysis of collisions with multiplicity larger than three is an exceedingly complicated problem and is the subject of an independent investigation.

We must, however, agree with Vdovin that the conclusions of[1] regarding the coexistence of non-mixing phases in a resonantly-excited gas, obtained on the basis of the virial expansions in the region where the latter are at the limit, are not sufficiently convincing. They should be regarded from the point of view of extrapolation of the theory beyond the framework of its applicability.

3. GAS OF METASTABLE EXCITED ATOMS

Assume that dipole transitions are forbidden between the ground state ϵ and the excited state ϵ', and assume further that the state ϵ is an S state, and the state ϵ' has nonzero orbital and total angular momenta. In this case the Q-Q interaction between the excited atoms differs from zero in the first perturbation-theory approximation. We shall henceforth consider only the interaction between the excited atoms, and then, on the basis of (1.16), the equation of state of such a gas with allowance for only pair interactions assumes the form

$$p = kT(n + n' - b_{02}n'^2), \quad (3.1)$$

$$b_{02} = \frac{1}{2gg'} \sum_s \int [e^{-\beta W_s(r)} - 1] d^3r,$$

$W_S = A_S/r^5$ is the energy of the Q-Q interaction of the excited atoms, calculated in first approximation of perturbation theory (the perturbation is the operator of the Q-Q interaction of the pair of excited atoms); s is a quantum number characterizing the state of the interacting atoms. The most interesting case corresponds to $A_S/r_0^5kT > 1$, in which the group integral can be calculated approximately:

$$b_{02} \approx \frac{4\pi r_0{}^3}{15g'^2} \sum_s \frac{r_0{}^5kT}{A_s} \exp\left\{\frac{A_s}{r_0{}^5kT}\right\}. \quad (3.2)$$

We proceed to numerical estimates of the group integral b_{02}. According to calculations performed in[4], the mean value is $A_S/r_0^5 \approx 2$ eV for atoms whose ground state is not an S state (r_0 can be approximately assumed equal to 2 Å). We should expect $W_S(r_0)$ to be at least of the same order for excited atoms. Rough estimates of $W_S(r_0)$ for excited atoms at $r_0 = 2$ Å lead to $W_S \sim 1$ eV. At room temperatures, the ratio $A_S/r_0^5kT \sim 8$. Retaining the term with the largest argument of the exponential in (3.2), we get $b_{02} \gtrsim 2.5 \times 10^{-22}$ cm^3.

It is of interest to compare the group integrals b_{02}, b_{11}, and b_{20}. In accordance with the data of[1], $b_{20} \approx 3.5 \times 10^{-24}$ cm^3, $b_{11} \approx 1.7 \times 10^{-19}$ cm^3. We see therefore that the corrections to the equation of state of the excited gas, due to Q-Q interaction between the metastable excited atoms, exceed the corrections due to the Van der Waals interaction. Thus, the Q-Q interaction turns out to be appreciable and makes an intermediate contribution to the thermodynamic functions, compared with the resonant D-D interaction and the ordinary Van der Waals interaction.

The author is grateful to S. I. Pekar for a discussion of the work.

APPENDIX

Let us change variables in b_{21} (formula (2.2)). This is conveniently done in two stages. We first use the Kihara variables[13]:

$$R = R_{12}, \quad R_{13} = R(x^2 + y^2)^{1/2}, \quad R_{23} = R[(1 - x)^2 + y^2]^{1/2},$$

with $R \geq R_{13}$ and $R \geq R_{23}$. We then change over from the integration variables x and y to the variables u and v in accordance with the formulas $x^2 + y^2 = u^2$ and $(1 - x)^2 + y^2 = v^2$, i.e., $R_{13} = Ru$ and $R_{23} = Rv$; $0 \leq u \leq 1$, $0 \leq v \leq 1$. After these transformations, b_{21} can be written in the following form:

$$b_{21} = \frac{4\pi^2}{3} \int_0^\infty R^5 dR \iint_{\{D\}} G(R, u, v)\, uv\, du\, dv. \quad (A.1)$$

Here G(R, u, v) is short hand for the integrand of (2.2) in terms of the variables R, u, and v, with allowance for the behavior of the functions $W_{S_{21}}$ and $W_{S_{11}}$ when $R < r_0$, $u < r_0/R$, $v < r_0/R$; {D} is the region of integration with respect to the variables u and v, as shown in Fig. 2.

Let us examine the contribution made to the group integral (A.1) by configurations in which all three atoms are separated from one another by distances larger than r_0. The contribution from the aforementioned configurations is best represented in the form of two integrals. The first is denoted by

$$I_1 = \frac{4\pi^2}{3} \int_{r_0}^{2r_0} R^5 dR \int_{r_0/R}^{1} \int_{r_0/R}^{1} \sum_{s=1}^{9} [\mathscr{E}_s(1,2,3) - \mathscr{E}_s(1,2)$$

$$- \mathscr{E}_s(1,3) - \mathscr{E}_s(2,3) + 2]\, uv\, du\, dv. \quad (A.2)$$

We have used here the previously employed notation for the quantities $\mathscr{E}_S$, and W_S (1, 2, 3) should be determined from Eqs. (2.6) and (2.7), while W_S (i, j) is given by formulas (2.8a). We denote the second integral by I_2, and its integrand coincides with the integrand of I_1, the limits of integration with respect to R being $2r_0$ and ∞. Integration with respect to u and v should be carried out in the region bounded by the straight lines $r_0/R \leq u \leq 1$, $r_0/R \leq v \leq 1$, $u + v = 1$ (Fig. 2). Thus, $b_{21} = I_1 + I_2$ + the contribution of configurations corresponding to interparticle distances smaller than r_0. The last term takes into account the contribution from the "proper volume" of the atoms. The integrals I_1 and I_2 cannot be evaluated

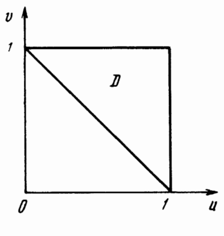

FIG. 2. Region of integration with respect to the variables u and v.

exactly, since there is no analytic relation for $W_S(R, u, v)$. Inasmuch as $A/r_0^3kT \sim 10 \gg 1$ in the case of greatest interest, the main contribution to b_{21} is made by configurations in which the atoms are brought close together to a distance of the order of r_0, i.e., $b_{21} \approx I_1$. Among the indicated configurations, the most significant ones are configurations of the linear-chain type. Therefore the integration with respect to the variables u and v should be carried out in the vicinity of the point $u = v = 1/2$, and the integration with respect to R in the vicinity of the point $2r_0$. In this region $W_S(R, u, v)$ are given with high accuracy by formulas (2.18). We retain in the integrand of (A.2) the exponential with the largest positive argument βW_S from (2.8). We expand the argument of the exponential in a series in the vicinity of $u = v = 1/2$, accurate to the linear terms, and obtain after integration

$$b_{21} \approx \frac{4\pi r_0^2}{3} \int_{r_0}^{2r_0} (R^3/128\alpha) \exp\left\{ \alpha \left[\frac{171}{R^3} - \frac{256 r_0}{R^4} \right] \right\} R^2 dR,$$
$$\alpha = \frac{4A \cos(\varphi/3)}{kT\sqrt{43}} \qquad \cos(\varphi/3) \approx 0{,}9 \quad (u = v = {}^1/_2). \tag{A.3}$$

The argument of the exponential has a maximum at $R = 1.99\, r_0$. In view of the presence of the factor $A/r_0^3kT \gg 1$, the main contribution to (A.3) is made by the vicinity of this maximum. Calculating (A.3) approximately by the Laplace method[14], we arrive at formula (2.10) of the main text.

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Translated by J. G. Adashko
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