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INTERMOLECULAR INTERACTION AND THE EQUATION OF STATE OF AN HIGHLY EXCITED GAS

V. N. MAL'NEV and S. I. PEKAR

Kiev State University

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It is shown that dipole-dipole interaction of two identical molecules at different energy levels which is inversely proportional to the cube of the distance does not vanish on averaging over all possible orientations of the molecular dipoles. This interaction yields a significant contribution to the thermodynamic functions and equation of state of an excited gas. It may be more important than the usual Van der Waals forces and result in deviation of the gas from perfection even at low pressures, and may also result in condensation of the gas. It is demonstrated that the excited gas may decompose into two phases with different relative amounts of excited molecules. One of the phases may condense and the excitation is then lifted by a nonradiative process; its equation of state changes and it evaporates again. This is a peculiar mechanism of conversion of electron excitation energy into heat. The processes considered here may be important in the operation of gas lasers.

A quantum theory of Van der Waal's forces was first developed by London and Eisenschitz[1] for the interaction of identical molecules, without account of retardation. Casimir and Polder[2] took retardation in the dipole-dipole interaction molecules into account, and showed that the retardation is significant and leads to a new result when the distance between molecules is of the order of or larger than the wavelength of the light that the given molecules can absorb. In the following years many papers, a review of which is given in[3,4], devoted to Van der Waal's forces.

In this article we consider a gas of sufficiently high molecule concentration (for example, at atmospheric pressure), when the average distance between molecules is much shorter than the wavelength of the light absorbed by these molecules, and when retardation can be neglected. Unlike earlier papers, we consider the case when a large percentage of the molecules is excited to the same electron energy level. This occurs, for example, when the gas is in an operating laser. In what follows, the interaction between the unexcited and excited molecules will be important. The energy of this interaction, as is well known, differs from zero even in the first perturbation-theory approximation, and is inversely proportional to the cube of the distance between molecules (the perturbation is the energy of the dipole-dipole interaction of the molecules). It is noted in the literature, however, that since this energy depends linearly on the matrix elements of the dipole moments of each molecule, it vanishes after averaging over all possible orientations of these moments. A nonzero contribution to the energy of the intermolecular interaction is given only by the second perturbation-theory approximation—an interaction inversely proportional to the sixth power of the distance r between the molecules.

Actually the interaction energy vanishes in the first perturbation-theory approximation if all the orientations of the matrix element of the dipole moments are assumed to be equivalent in the averaging. A more correct averaging, however, which takes into account the correlation of the mutual orientations of the virtual dipole, will show below that the main contribution to the partition function of the gas can be made by precisely the first-approximation energy, which is proportional to r^{-3}.

The calculations that follow pertain to the case of monatomic molecules, and a very simple example is used to illustrate the singularities inherent in a highly excited gas: the anomalously large interaction energy, proportional to r^{-3}, between molecules in different electronic states, and the corresponding deviation of the gas from ideal at relatively low concentrations.

1. PARTITION FUNCTION OF ATOMIC EXCITATION OF A REAL GAS

Let $\mathcal{R}$ be the aggregate of the coordinates of the electrons of the entire gas, $R(\ldots\mathbf{R}_j\ldots)$ the aggregate of the coordinates of the centers of gravity of the atoms, and $\mathbf{R}_j$ the three dimensional vector of the position of the center of gravity of the j-th atom. The energy operator of the entire gas is

$$H = T(R) + \mathcal{H}(\mathcal{R}, R), \tag{1}$$

where T(R) is the operator of the kinetic energy of the translational motion of the atoms, and $\mathcal{H}(\mathcal{R}, R)$ is the operator of the energy of the motion of the electrons inside the atom and the potential energy of the interaction between the atoms. $\mathcal{H}(\mathcal{R}, R)$ does not contain differential operations with respect to $\mathbf{R}_j$.

We determine the partition function of the gas from the formula $Z = \mathrm{Sp}\exp(-\beta H)$ ($\beta = 1/kT$), and calculate the trace with the complete system of functions

$$\Psi_{sk} = V^{-N/2} \prod_{j=1}^{N} e^{i\mathbf{k}_j\mathbf{R}_j}\Psi_s(\mathcal{R}, R), \tag{2}$$

where N is the number of gas atoms, V the gas volume, Ψ_s the eigenfunction of the operator $\mathcal{H}(\mathcal{R}, R)$: $\mathcal{H}\Psi_s = E_s(R)\Psi_s$. Here $E_s(R)$ is the total energy of the electron motion of the gas, calculated at fixed atom positions, and s is the aggregate of the electron quantum numbers. As usual, in determining the energy of the intermolecular interaction we assume that the electron motion over the degrees of freedom of $\mathcal{R}$ follows adiabatically the relatively slow changes of R.

The calculation yields

$$Z = \sum_{sk} \langle \Psi_{sk} | e^{-\beta H} | \Psi_{sk} \rangle = Z_0 \sum_s \int e^{-\beta E_s(R)}\, dR, \tag{3}$$

$$Z_0 = \left(\frac{MkT}{2\pi\hbar^2}\right)^{3N/2}.$$

Here M is the mass of the atom.

It is convenient to put $E_s(R) = E_s^0 + W_s(R)$, where E_s^0 is the energy of the noninteracting atoms and $W_s(R)$ the energy of their interaction ($W_s(R) \to 0$ as $|\mathbf{R}_i - \mathbf{R}_j| \to \infty$). Let us assume that the concentration of the atoms is small and therefore it is necessary to take into account in the partition functions only paired interactions of the atoms. We assume further that in integrating in (3) with respect to R we can neglect the small volume corresponding to configurations at which more than two atoms interact. Then, putting $W_s(R) = \sum_{i<j} W_{s_{ij}}(\mathbf{R}_i \cdot \mathbf{R}_j)$ and introducing the relative coordinates $\mathbf{R}_i - \mathbf{R}_j = \mathbf{r}$, we obtain

$$Z = Z_{\mathrm{id}} + Z_0 V^{N-1} \sum_s e^{-\beta E_s^0} \sum_{i<j} \int \left(e^{-\beta W_{s_{ij}}(r)} - 1\right) d^3r, \tag{4}$$

where Z_{id} is the partition function of the ideal gas:

$$Z_{\mathrm{id}} = V^N Z_0 \sum_s e^{-\beta E_s^0}, \tag{5}$$

s_{ij} is the aggregate of quantum numbers of the electrons belonging to the interacting i-th and j-th atoms.

We assume that there are two species of atoms in the gas, with two electron energies ϵ and ϵ' respectively (both atoms are of the same chemical element). Let the number of atoms of the first species be N and of the second N′.

It must be emphasized that the presence in the gas of atoms with only two values of electron energy denotes that the gas is not in thermal equilibrium, and the question arises whether the calculation of its partition function is valid. It is possible, however, to justify the calculation of such a partition function with fixed atom numbers N and N′ whose ratio has nothing in common with equilibrium statistics. The point is that the relaxation time needed to establish thermal equilibrium with respect to the translational motion of the atoms is of the order of 10^{-10} sec (atmospheric pressure, room temperature); the electron energy, on the other hand, changes within a much longer time, on the order of 10^{-8} sec, and the time for the transition of the electron excitation energy into the energy of translational motion of the atoms is larger still by many orders of magnitude. Therefore at nonequilibrium values of the electron energy there is time for equilibrium to become established in the translational motion of the atoms, and the corresponding partition function can be calculated. This equilibrium may even be stationary in time, provided the electron energies ϵ and ϵ' and the atom N and N′ numbers are maintained constant by external action of the gas. Such an action can be, for example, illumination of the gas, producing a constant number of excited atoms with a given electron energy (optical pumping of a gas laser).

After making the foregoing assumptions, the partition function (4) can be rewritten in the form

$$Z = Z_{\mathrm{id}}\left[1 + \frac{N^2}{V}B_1(T) + \frac{NN'}{V}B_2(T) + \frac{N'^2}{V}B_3(T)\right], \tag{6}$$

where

$$2B_1 = g^{-2} \sum_{s_{12}} \int \left[e^{-\beta W_{s_{12}}} - 1\right] d^3r, \tag{7}$$

$$B_2 = (2gg')^{-1} \sum_{s_{11'}} \int \left[e^{-\beta W_{s_{11'}}} - 1\right] d^3r, \tag{8}$$

$$2B_3 = g'^{-2} \sum_{s_{1'2'}} \int \left[e^{-\beta W_{s_{1'2'}}} - 1\right] d^3r. \tag{9}$$

Here s_{12} numbers the electronic states of the pairs of atoms, each of which has in the zeroth approximation (without account of the interaction) an energy ϵ, and $W_{s_{12}}$ is the interaction energy of these atoms; $s_{11'}$ numbers the electronic states of a pair of atoms with energies ϵ and ϵ' in the zeroth approximation, and $W_{s_{11'}}$ is their interaction energy; $s_{1'2'}$ numbers the electronic states of a pair of atoms with energies ϵ', and $W_{s_{1'2'}}$ is the interaction energy of these atoms; g and g′ are the atomic degeneracy multiplicities of the electronic states with energies ϵ and ϵ'.

We proceed to calculate the atom-pair interaction energy. The interaction-energy operator of two atoms has in the dipole-dipole approximation the form

$$W = r^{-3}[\mathbf{p}_1\mathbf{p}_2 - 3p_{1z}p_{2z}], \tag{10}$$

where $\mathbf{p}_1$ and $\mathbf{p}_2$ are the dipole moments of the atoms. We choose the oz axis along the line joining the two atoms.

If the two atoms have identical electron energies (ϵ or ϵ'), then the correction to the energy, due to the perturbation (10), vanishes in first approximation for all the atoms except hydrogen atoms. On the other hand, if two hydrogen atoms with identical electron energies interact, and these atoms are not in the ground state, then among the degenerate electron states of each atom there will be states with different azimuthal quantum numbers. Therefore, in accordance with the well known selection rules, some off-diagonal matrix elements of the perturbation (10) will differ from zero and the roots of the corresponding secular equation, i.e., $W_{s_{12}}(r)$, will differ from zero. Thus, for hydrogen consisting of identically excited atoms, the energy of interatomic interaction is

$$W_{s_{12}}(r) = A_{s_{12}}/r^3. \tag{11}$$

A similar interaction, proportional to r^{-3}, is obtained in the case of two atoms of the same element but with different electron energies. Indeed, assume that the atom with energy ϵ has degenerate electron states $\psi_1, \psi_2, \ldots, \psi_n, \ldots, \psi_g$, and the atom with energy ϵ' has states $\varphi_1, \varphi_2, \ldots, \varphi_{n'}, \ldots, \varphi_{g'}$. Then the system of two atoms has in the zeroth approximation an energy $\epsilon + \epsilon'$, and this energy corresponds to 2gg′ degenerate functions

$$\begin{aligned} \Psi_\alpha &= \psi_n(1)\varphi_{n'}(2), \quad \alpha = 1, 2, \ldots, gg'; \\ \Psi_\alpha &= \psi_n(2)\varphi_{n'}(1), \quad \alpha = gg'+1, \ldots, 2gg'. \end{aligned} \tag{12}$$

The number 1 stands here for the set of coordinates of the electrons of the first atom, and 2 for the set of coordinates of the electrons of the second atom. The matrix elements $W_{\alpha_1\alpha_2}$ of the perturbation (10), calculated with the aid of the functions (12), differ from zero only when $1 \le \alpha_1 \le gg'$ and $gg' + 1 \le \alpha_2 \le 2gg'$, or else when $gg' + 1 \le \alpha_1 \le 2gg'$ and $1 \le \alpha_2 \le gg'$. Thus, the secular equation which determines $W_{s_{11'}}(r)$ has the following form: $\det|W_{\alpha_1\alpha_2} - W_{s_{11'}}\delta_{\alpha_1\alpha_2}| = 0$. Its solution will be written in the form $W_{s_{11'}} = A_{s_{11'}}/r^3$.

If two atoms (not of hydrogen) with identical electron energies interact, then the energy of their interaction differs from zero in the second perturbation-theory approximation:

$$W_{s_{12}}(r) = C_{s_{12}}/r^6. \tag{13}$$

In this case forces of the ordinary Van der Waal type arise, but the constant $C_{s_{12}}$ can have either sign in the case of excited atoms.

In all cases when r becomes of the order of double the atomic radius or less, the dipole-dipole approximation fails, the exchange forces neglected above come into play, and repulsion sets in between the atoms, increasing as the atoms come close together. We assume for simplicity, as is customary, that $W_{s_{ij}} = \infty$ when $r < r_0$, and that $W_{s_{ij}}$ is determined by formulas (11) or (13) when $r > r_0$.

We now proceed to calculate the integrals in (7)—(9). It must be borne in mind here that $\sum_{s_{ij}} A_{s_{ij}} = 0$. This is proved in the mathematical appendix. Introducing the symbol $a_s = A_{s_{11'}}/r_0^3kT$, it is possible to carry out the integration in (8) exactly and we get

$$B_2 = \frac{2\pi r_0^3}{3gg'} \sum_s \{a_s[\ln|a_s| - \mathrm{Ei}(-a_s)] - e^{-a_s}\}. \tag{14}$$

Here Ei is the integral exponential function. Thus, an interaction proportional to r^{-3} gives a nonzero contribution to the coefficient function (16) and to the other thermodynamic functions.

Substituting (13) in (7) and (9), and introducing the notation $c_s = C_{s_{12}}/r_0^6kT$, we obtain after integration

$$B_1 = \frac{2\pi r_0^3}{3g^2} \sum_s [2\sqrt{c_s}\, y(\sqrt{c_s}) - e^{c_s}], \qquad y(x) = \int_0^x e^{t^2}\,dt. \tag{15}$$

A similar expression is obtained also for B_3. In the case of identical excited hydrogen atoms we obtain for B_3 expressions of the type (14). Inasmuch as the parameter r_0 plays an important role in (14) and (15), these formulas enable us only to estimate B_1 and B_2. On the other hand, these formulas are exact for the model with the form of $W_{s_i}(r)$ chosen above.

In the case of high temperatures, when $|a_s| \ll 1$ or $|c_s| \ll 1$, formulas (14) and (15) go over respectively into

$$B_2 = \frac{2\pi r_0^3}{3gg'} \sum_s \left[-1 + \frac{a_s^2}{2!} + \ldots \right], \tag{16}$$

$$B_1 = \frac{2\pi r_0^3}{3g^2} \sum_s [-1 + c_s + \ldots]. \tag{17}$$

In these formulas the brackets contain the term -1, from which we obtain in the Van der Waals equation the term of the "proper volume of the molecules" b, which does not depend on the temperature and on the law governing the interaction of the molecules at large distances. The second terms in the brackets, $-a_s^2/2!$ and c_s, are both proportional to r_0^{-6} and generate in the Van der Waals equation the "internal pressure" term (N^2a/V^2). An estimate of these terms yields

$$a_s \sim e^2 |x_{nl}|^2 / r_0^3 kT, \qquad c_s \sim e^4 |x_{nl}|^4 / r_0^6 kT (\varepsilon_1 - \varepsilon_2),$$

where r_0 is the radius of the atom (not necessarily in the ground state), and $\epsilon_1 - \epsilon_2$ is the energy of the electron transition having the dominating oscillator strength. Thus, the ratio of the two aforementioned terms is equal to

$$\frac{a_s^2}{2c_s} \sim \frac{\varepsilon_1 - \varepsilon_2}{kT}. \tag{18}$$

Since $\epsilon_1 - \epsilon_2$ can be of the order of several electron volts, at room temperature the ratio (18) can be of the order of several hundred. The Van der Waals coefficient a for differently excited atoms will be larger by the same factor than for atoms with identical electron energy. Incidentally, it must be emphasized that so long as $|a_s| \ll 1$ and $|c_s| \ll 1$, the internal-pressure term in the Van der Waals equation is negligibly small compared with the pressure in both cases.

In the case of low temperatures, i.e., when $-a_s \gg 1$ or $c_s \gg 1$, formulas (14) and (15) go over into

$$B_2 = \frac{2\pi r_0^3}{3gg'} \sum_s \frac{e^{-a_s}}{-a_s}, \tag{19}$$

$$B_1 = \frac{\pi r_{03}}{3g^2} \sum_s \frac{e^{c_s}}{c_s}. \tag{20}$$

With decreasing temperature, $|a_s|$ and $|c_s|$ increase like T^{-1}. The ratio (18), however, remains much larger than unity, therefore the case occurring first without fail is $|a_s| \gg 1$, $|c_s| \ll 1$, when the interaction of the atoms of like species (the terms with B_1 and B_3 in (6)) can be neglected in the calculation of the internal pressure, but account must be taken of the interaction of atoms of unlike species (the term with B_2 in (6)). The case $|c_s| \gg 1$ occurs only if the temperature is lowered further.

In the estimates we shall express the matrix element of the coordinate x_{nl} in terms of the oscillator strength f_{nl}, using the formula $|x_{nl}|^2 = \hbar f_{nl}/2m\omega_{nl}$, where ω_{nl} is the transition frequency $(\omega_{nl} = (\epsilon_1 - \epsilon_2)/\hbar)$. Then

$$a_s \sim \frac{1}{2}\left(\frac{a_0}{r_0}\right)^3 \frac{(me^4/\hbar^2)^2 f_{nl}}{\hbar\omega_{nl} kT}, \tag{21}$$

where $a_0 = \hbar^2/me^2 = 0.529$ Å is the radius of the hydrogen atom. As a numerical example let us consider the case $\hbar\omega_{nl} = 2$ eV, $f_{nl} = 0.1$, $r_0 = 4a_0$, and $T = 300°K$. Then $a_s = -11.5$ and $V_2 = 1.74 \times 10^{-19}$ cm^3. For the same data we obtain from (18) $c_s = 0.825$, and from (17) $B_1 = 3.5 \times 10^{-24}$ cm^3. Thus, in the example considered here, the interaction of atoms of like species (ordinary Van der Waals forces), represented by the term with B_1 in (6), is negligibly small compared with the term with B_2, which x describes the interaction of differently excited atoms, which is proportional to r^{-3}. For example, at atmospheric pressure the term with B_1 does not lead to any noticeable deviation from an ideal gas, whereas the term with B_2 creates appreciable deviations, as will be shown below.

Taking (3), (5), and (6) into account, we obtain for a mixture of atoms of both species the partition function

$$Z = \frac{1}{N!}\left[V\left(\frac{MkT}{2\pi\hbar^2}\right)^{3/2} g e^{-\varepsilon/kT}\right]^N \frac{1}{N'!}\left[V\left(\frac{MkT}{2\pi\hbar^2}\right)^{3/2} g' e^{-\varepsilon'/kT}\right]^{N'}$$
$$\times \exp\left\{\frac{(N^2B_1 + NN'B_2 + N'^2B_3)}{V}\right\}. \tag{22}$$

The division by N! and N'! is connected here with the identity of the atoms of these species.

2. EQUATION OF STATE AND EXISTENCE OF TWO PHASES OF HIGHLY-EXCITED GAS

The free energy of a mixture of atoms of two species is calculated from (22) by means of the formula

$$F = -kT \ln Z. \tag{23}$$

We shall henceforth neglect the usual Van der Waals forces, but will take into account an interaction proportional to r^{-3} between atoms of different species. Accordingly, we shall discard the terms with B_1 and B_3 in the argument of the exponential in (22). Then the pressure of the mixture of atoms is equal to

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = kT\left[\frac{N + N'}{V} - \frac{NN'}{V^2}B_2\right]. \tag{24}$$

This equation of state shows that at room temperature, if the Lohschmidt concentration of the atoms of the first species is $N/V = L = 2.55 \times 10^{19}$ cm^{-3}, and if $N' = 0.1$ N and $B_2 = 1.74 \times 10^{-19}$ cm^3, then the second term in (24) is equal to half the first term. Thus, the pressure of the mixture will be equal to 0.5 atm, whereas in the case of an ideal gas it would be equal to 1 atm at the same temperature and concentration of the atoms. Consequently, a large deviation from an ideal gas takes place even at a 10% content of atoms of the second species (excited atoms).

A pressure of 0.5 atm, at which the second term in (24) amounts to half the first term, is precisely the maximum of the function p(V). When the volume decreases, the pressure also begins to decrease, instability sets in, and the gas condenses into a liquid. Thus, a 10% content of excited atoms in a gas can lead to condensation under conditions at which the unexcited gas would be almost ideal. This singularity must be taken into account in the construction of gas lasers.

It can be shown that the large deviations from ideal behavior considered above (but of course not the condensation) occur in the region where the approximation of paired interactions of the atoms is still valid. The reason is that in the case of the dipole-dipole interaction proportional to r^{-3}, which was considered above, the binding energy of a group of several closely-lying atoms does not exceed, for the most part, the binding energy of a pair of atoms of different species. Thus, if the number of atoms of one species approaches the number of atoms of the other species, then the binding energy of the latter group of atoms will be smaller than or equal to the binding energy of an atom pair consisting of an atom of the second species and the nearest atom of the first species[1)]. Therefore, this group of closely spaced atoms makes a much smaller contribution to the configuration integral of formula (3) than the aforementioned atom pair. It can be further shown that if the group of the closely spaced atoms contains two atoms of one species and any number of atoms of the other species, then the binding energy of this group does not exceed the sum of the binding energies of the two pairs of the closest atoms, etc.

We proceed now to investigate the possible existence of nonmixing and spatially separated phases of the considered gas mixture. The question of the decomposition of a mixture of two real gases into two nonmixing gas phases was theoretically considered already by Van der Waals[5,6]. Experimentally, such a decomposition was observed by Krichevskiĭ, Bol'shakov, and Tsiklis[7-9]. Similar questions were investigated theoretically in recent times by Rott[10], Temkin[11], and others.

In all the foregoing investigations, the decomposition of a mixture of gases into two phases turned out to be possible only at high pressures (hundreds and thousands of atmospheres). On the other hand, in the case of an excited gas which we are considering, owing to the anomalously large intermolecular forces, decomposition into two different phases may turn out to be possible at atmospheric or even lower pressures, and one of the phases may become condensed.

Let us consider one mole of our gas mixture, $N + N' = N_0$, where N_0 is the Avogadro number. The ratio of the mixture components is characterized by $x = N'/N_0$. The mixture volume determined from (24) is expressed as a function of the pressure by the formula

$$V(p) = \frac{RT}{2p}[1 \pm \sqrt{1 - 4\gamma x(1-x)}], \qquad \gamma = \frac{pB_2N_0}{RT}. \quad (25)$$

Here R is the Clapeyron constant. We shall always take the plus sign in front of the square root, since we wish to confine ourselves to the stability region, in which $\partial p/\partial V < 0$. According to (23) and (25), the thermodynamic potential of the mixture is given by the formula

$$\Phi = RT\left[x \ln x + (1-x)\ln(1-x) - \ln V(p) - \frac{B_2}{V(p)} N_0 x(1-x)\right] + pV(p) + \alpha, \quad (26)$$

where

$$\alpha = \alpha_1 x + \alpha_2, \quad \alpha_1 = RT \ln(g/g') + N_0(\varepsilon' - \varepsilon),$$
$$\alpha_2 = N_0\varepsilon + RT \ln\left[\frac{N_0}{eg}\left(\frac{2\pi\hbar^2}{MkT}\right)^{3/2}\right], \quad (27)$$

e is the base of the natural logarithms. Expression (26) is the thermodynamic potential of a spatially homogeneous single-phase system containing x moles of excited gas and (1 − x) moles of unexcited gas.

The decomposition of the mixture into two different nonmixing phases, as is well known[5,6], occurs if $\partial^2\Phi/\partial x^2 < 0$. In this case the compositions of the resulting phases (x_a and x_b), the number of moles of phase a(μ), the number of moles of phase b ($1 - \mu$) and the thermodynamic potential of the two-phase system (Φ_{ab}) are best determined graphically, as shown in Fig. 1. In this figure the curve shows the thermodynamic potential of the single-phase non-decomposing system plotted against its composition x. The state of this initial system is

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[1)] Smaller, if the electron excitation migrates exciton-like between the atoms of the group: equal, if the excitation is localized on the aforementioned pair of atoms. When $|a_s| >> 1$, the only actual state is the state s at which the binding energy of the group is maximal.

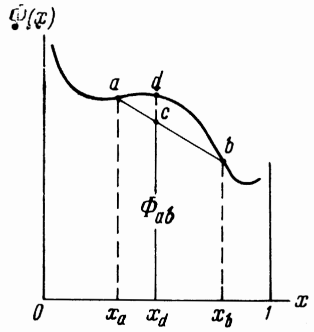

FIG. 1. Dependence of the thermodynamic potential of the component system on its composition x.

represented by the point d. The states resulting from the decomposition of the phases are represented by points a and b. The thermodynamic potential of the two-phase system is equal to Φ_{ab} ($\Phi_{ab} < \Phi(x_d)$). The value of μ is determined from the relation

$$\mu(x_d - x_a) = (1 - \mu)(x_b - x_d). \tag{28}$$

The point c is the center of gravity of the masses μ and $1 - \mu$, placed at the points a and b respectively. Equilibrium, i.e., the minimum of the function Φ_{ab}, corresponds to the lowest possible position of the chord, at which the points a and b become tangency points[6].

Returning to the system considered by us, we note that when $\gamma \leq 1$ decomposition into two phases is impossible, since $\partial^2\Phi/\partial x^2 > 0$ for all x if $\Phi(x)$ is defined by formulas (25) and (26). When $\gamma > 1$, the radicand of (25) is negative in the middle region of x. This means that the maxima of the isotherms shown in Fig. 2 lie below the straight line p = const (see Fig. 2, Curve III). In this case the gas condenses into a liquid, the state of which is represented by the point f in Fig. 2. This state lies beyond the limits of applicability of this theory.

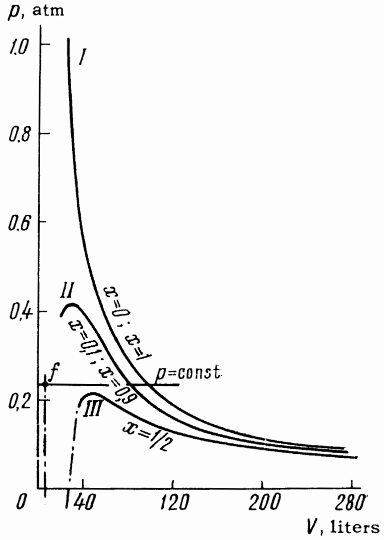

FIG. 2. Dependence of p on V for different values of x. $B_2 = 1.74 \times 10^{-19}$ cm³, T = 273°K.

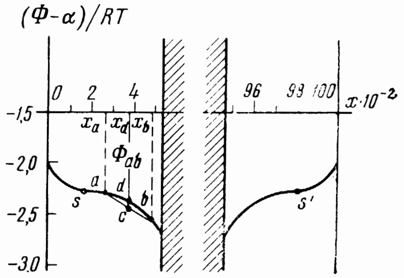

FIG. 3. Dependence of the thermodynamic potential of excited gas on x. $B_2 = 1.74 \times 10^{-19}$ cm³, T = 273°K, $\gamma = 5$.

The curve of Fig. 3 represents a plot of $\Phi - \alpha$, determined by formulas (26) and (27), against x. The cross hatching marks the area in which the radicand of (25) is negative, i.e., the gas condenses into a liquid. Since α is a linear function of x, $\Phi - \alpha$ has the same second derivative with respect to x as $\Phi(x)$. It can be shown that the graphic method illustrated above by Fig. 1 with a plot of $\Phi(x)$, is valid in the same form also for a plot of $\Phi(x) - \alpha(x)$. It thus follows from Fig. 3 that a spatially homogeneous gas mixture, initially represented by the point d, can decompose with a decrease in the thermodynamic potential into two different phases represented by the points a and b. On approaching equilibrium and further decrease in Φ_{ab}, the chord ab should move in such a way that the point c drops. Then the point b goes into the shaded region, i.e., the phase b condenses.

Actually the condensation can occur even before the point b enters into the shaded region, since the condensation plateau of the "real isotherms" lies below the maximum of the theoretical isotherms shown in Fig. 2.

When the excited gas condenses, the interaction between the atoms becomes stronger and nonradiative transitions of the electrons to the ground state begin. Then the value of x in the condensate decreases, and the condensate again evaporates. Such a process is a unique mechanism of deexciting the gas.

If the composition of the initial spatially-homogeneous gas mixtures is represented by a point lying on the right of the cross-hatched strip in Fig. 3, then the decomposition will cause condensation of the phase with the smaller x, the gaseous phase will have larger x, and x will then increase, i.e., the relative number of excited atoms will increase.

The foregoing mechanism of deexciting the gas and its repeated evaporation can greatly influence the operating conditions of a gas laser. These processes do not occur if the state d of the initial homogeneous mixture of the gases is located to the left of the inflection point s or to the right of the inflection point s′, since $\partial^2\Phi/\partial x^2 > 0$ in these regions.

APPENDIX

Formula (11) constitutes a correction to the energy in first approximation of the perturbation (10), calculated with the zeroth-approximation wave functions (12). Therefore the $A_{s_{ij}}$ are determined from the secular equation

$$|\langle\alpha_1|\mathbf{p}_1\mathbf{p}_2 - 3p_{1z}p_{2z}|\alpha_2\rangle - \delta_{\alpha_1\alpha_2}A_{s_{ij}}| = 0.$$

As is well known, the sum of the roots of this secular equation is equal to the trace of the matrix $\langle\alpha_1|\mathbf{p}_1\cdot\mathbf{p}_2 - 3p_{1z}p_{2z}|\alpha_2\rangle$ or the sum of the diagonal matrix elements of the perturbation (10), calculated with the wave functions (12):

$$\sum_{s_{ij}} A_{s_{ij}} = \sum_{\alpha}\langle\alpha|\mathbf{p}_1\mathbf{p}_2 - 3p_{1z}p_{2z}|\alpha\rangle.$$

but each diagonal matrix element $\langle\alpha|\mathbf{p}_1\cdot\mathbf{p}_2 - 3p_{1z}p_{2z}|\alpha\rangle$ is equal to zero (see the remark following (12)). Therefore $\sum_{s_{ij}} A_{s_{ij}} = 0$.

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218