4. It is shown that at T_λ there should be observed a discontinuity in the heat of mixing and a discontinuity in the heat of vaporization. A numerical value for the magnitude of the discontinuity in the heat of mixing has been obtained for weak mixtures. For one of these mixtures the temperature dependence of the heat of mixing has been calculated. The dependence of the heat of transition upon the concentration of the phase being formed has been calculated for various temperatures.

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ON THE EQUATIONS OF THE OSCILLATIONS OF THE MOLECULAR GENERATOR

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By use of a density matrix in the proper approximation, equations are derived that describe both stationary and nonstationary operating conditions of the molecular generator.

THE theoretical problems connected with the molecular generator have been discussed by several authors.[1-3] In these articles, however, only stationary or nearly stationary operating conditions are described. It is of interest to derive equations of the molecular generator that are valid for arbitrary operating conditions.

Upon replacing the resonant cavity by an equivalent circuit it is not difficult to derive the following equation, which describes the oscillations in the circuit:

$$\ddot{E} + 4\pi\ddot{P} + (\omega_0 / Q)(\dot{E} + 4\pi\dot{P}) + \omega_0^2 E = 0. \tag{1}$$

Here E is the electric field intensity, P is the polarization of the medium in the resonant cavity, Q is the figure of merit of the circuit, and ω_0 is the natural frequency of the circuit. Equation (1) is still insufficient to describe the operation of the molecular oscillator. It remains to find equations that connect E with P.

In Refs. 1 to 3 and others it is assumed that E depends on the time harmonically (with frequency ω), and in this case the relation between E and P is given in a certain approximation. However, because the relation between E and P is nonlinear (saturation effect), summation over all frequencies ω does not lead to a general relation between E and P. The goal of the present work is to find such a relation.

Molecules in the presence of an alternating electric field E(t), like any other quantum-mechanical system, are described by a density matrix $\hat{\rho}$. The latter in our case obeys the equation

$$i\hbar\partial\hat{\rho}/\partial t = H\hat{\rho} - \hat{\rho}H, \tag{2}$$

where

$$H = H_0 - \hat{\mu}E, \tag{3}$$

H_0 is the Hamiltonian of the free (without field) molecule, and $\hat{\mu}$ is the operator for the dipole moment of the molecule.

The polarization, i.e., the average dipole moment of the gas per unit volume, is given by

$$P = \mathrm{Sp}\,(\hat{\rho}\hat{\mu}). \tag{4}$$

Here $\hat{\rho}$ is referred to unit volume. At a given instant of time t the contribution to the polarization P (as well as to $\hat{\rho}$) comes from those molecules which entered the resonator at a time $t_0 = t - \theta$; the largest contribution is made by molecules for which $\theta \lesssim \tau$, where τ is the average time of flight of a molecule across the resonant cavity. Hence we are interested in the average value of $\hat{\rho}$ obtained as follows:

$$\hat{\rho}(t) = \int_0^\infty \hat{\rho}(t, t_0 = t - \theta)\, f(\theta)\, d\theta, \tag{5}$$

where $f(\theta)$ is a function that has been normalized to unity and decreases rapidly enough for $\theta > \tau$. The problem is simplified considerably if $f(\theta)$ is taken in the form

$$f(\theta) = (1/\tau)\, e^{-\theta/\tau}. \tag{6}$$

Such an approximation was used by Basov and Prokhorov* (Ref. 1).

It is easy to show by use of (2), (5), and (6) that $\hat{\rho}$ (t) satisfies the equation

$$\partial\hat{\rho}/\partial t = (-i/\hbar)(H\hat{\rho} - \hat{\rho}H) - \tau^{-1}(\hat{\rho} - \hat{\rho}_0). \tag{7}$$

Here $\hat{\rho}_0 \equiv \hat{\rho}(t, t_0 = t)$ is the density matrix at the instant of entry of the molecules into the resonator.

Now we assume that the molecule has only two levels E_1 and E_2 ($E_2 > E_1$). Then $\hat{\rho}$ is a two-rowed matrix. Further we assume that at the instant of entry into the resonator all molecules are in the state E_2. Then

$$(\rho_0)_{11} = (\rho_0)_{12} = (\rho_0)_{21} = 0; \quad (\rho_0)_{22} = N_0, \tag{8}$$

where N_0 is the number of active molecules per unit volume in the absence of the field.

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*Strictly speaking, in a molecular beam (which is used in the molecular generator) P is a function of z and v

$$P = P(t;\, t - z/v),$$

where the z axis is along the beam, and v is the velocity of molecules in the beam. When we replace the resonator by the equivalent circuit, it is necessary to average P along z as follows [cf., e.g., Ref. 4],

$$P(t, v) = \int P(t, t - z/v)\, E_a(z)\, dz,$$

where $E_a(z)$ is the normal oscillation of the cavity. Next, this formula should be averaged over v. However, even the monochromatic approximation leads to rather cumbersome equations.

In the representation, in which H_0 is diagonal and has eigenvalues E_1 and E_2, Eq. (7) can be written in the form

$$\dot{\rho}_{12} + i(\omega_{12} + \tau^{-1})\rho_{12} = \frac{i}{\hbar}(\rho_{22} - \rho_{11})E\mu_{12}, \quad \dot{\rho}_{21} + (i\omega_{21} + \tau^{-1})\rho_{21} = -\frac{i}{\hbar}(\rho_{22} - \rho_{11})E\mu_{21},$$

$$\dot{\rho}_{11} = \frac{i}{\hbar}E(\mu_{12}\rho_{21} - \rho_{12}\mu_{21}) - \tau^{-1}\rho_{11}, \quad \dot{\rho}_{22} = \frac{i}{\hbar}E(\mu_{21}\rho_{12} - \rho_{21}\mu_{12}) - \tau^{-1}(\rho_{22} - N_0). \tag{9}$$

From (4) we find (assuming that $\mu_{11} = \mu_{22} = 0$)

$$P = \rho_{12}\mu_{21} + \rho_{21}\mu_{12}. \tag{4a}$$

From (9) and (4a) it is not difficult to derive (taking into account that $\omega_{21} = -\omega_{12} \equiv \omega_2 > 0$)

$$\ddot{P} + (2/\tau)\dot{P} + (\omega_2^2 + \tau^{-2})P = -2NE|\mu_{12}|^2\omega_2/\hbar, \quad \dot{N} + \tau^{-1}N - (2/\hbar\omega_2)E(\dot{P} + \tau^{-1}P) = \tau^{-1}N_0. \tag{10}$$

These are the desired equations connecting E and P; hence in these equations N stands for the number of active molecules in the presence of the field E: $N = \rho_{22} - \rho_{11}$ (for $E = 0$ and $N = N_0$).

If we set $E = E_0 \cos \omega t$, then it is easily shown from Eqs. (10) that under neglect of higher harmonics and for ω close to ω_2 an expression for the complex dielectric constant is obtained that takes into account the saturation effect and agrees with the expression derived in Ref. 1.

Thus a complete system of equations, describing the oscillation of the molecular generator, is given by Eqs. (1) and (10).

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