CALCULATION OF THE VOLUME CONCENTRATIONS OF DOUBLE MOLECULES IN SATURATED AND SUPERHEATED MERCURY VAPOR FROM EXPERIMENTAL DATA ON THE SPEED OF SOUND

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Allowance for dimerization in alkali metal and mercury vapor is necessary in calculating the thermodynamic functions. At present calculation of the concentrations of double molecules in alkali metal vapors is based on the dimerization energy at absolute zero D_0. In this case one must take into account the fact that, to a large extent, the calculated number of double molecules depends on the assumed value of the dimerization energy. Even a relatively small error in the value of D_0 has a considerable effect on the percentage content of double molecules [1]. Below it is shown how the number of double molecules may be calculated from experimental data on the speed of sound.

We shall consider the metal vapor as an equilibrium mixture of two chemically reacting ideal gases—one monatomic and one diatomic. Moreover, we shall assume that when the sound wave is propagated thermodynamic equilibrium can be established at any point and at any time. Then for the thermodynamic speed of sound in superheated and saturated (with approach to the saturation line from the single-phase region) dissociating vapor we have the expression [2]

$$c = \left(g\frac{C_p}{C_v(1+\xi)}pv\right)^{1/2} = \left(g\frac{C_p}{C_v(1+\xi)}R_\times T\right)^{1/2}, \quad \left(\xi = \frac{\alpha(1-\alpha)}{2}\right). \quad (1)$$

Here α is the degree of dissociation (the subscript "×" means that the quantities relate to the mixture). Let p_1, p_2 be the partial pressures, and x_1, x_2 the volume concentrations of the monatomic and diatomic components. Then

$$p_1 + p_2 = p, \quad X_1 + X_2 = 1, \quad X_1 = p_1/p,$$
$$X_2 = p_2/p, \quad \alpha = (1 - X_2)/(1 + X_2).$$

We will express the quantities in Eq. (1) in terms of x_2. The volume concentration is numerically equal to the molar concentration, i.e., $x_i = M_i/M$, where M_i is the number of moles of the i-th component, M is the total number of moles for the mixture as a whole.

Volume Concentrations of Double Molecules in Saturated and Superheated Mercury Vapor

t°, C	X_2, %	t°, C	X_2, %	t°, C	X_2, %
Isobar 0.05 kg/cm²		370	0.09	Isobar 0.7 kg/cm²	
224.5	1.74	400	0.02	335.9	2.29
230	1.06	Isobar 0.16 kg/cm²		340	1.66
240	0.66	268.0	1.95	350	1.18
250	0.45	270	1.6	360	0.85
260	0.29	280	1.1	380	0.35
270	0.18	290	0.8	400	0.07
280	0.12	300	0.62	Isobar 1.1 kg/cm²	
300	0.06	330	0.30	361.3	2.4
330	0.05	370	0.09	370	1.1
360	0.03	400	0.03	380	0.69
400	0.01	Isobar 0.3 kg/cm²		390	0.4
Isobar 0.07 kg/cm²		294.4	2.08	400	0.18
235.9	1.8	300	1.5	Isobar, 1.5 kg/cm²	
240	1.35	310	1.1	377.8	2.5
250	1.05	320	0.85	380	1.5
260	0.71	330	0.65	390	0.73
270	0.52	350	0.34	400	0.4
280	0.39	370	0.15		
300	0.20	400	0.05		
330	0.11				

For the apparent molecular weight of the mixture we can write

$$\mu_\times = \frac{G}{M} = \frac{G_1+G_2}{M} = \frac{M_1\mu_1 + M_2\mu_2}{M} =$$
$$= X_1\mu_1 + X_2\mu_2 = (1-X_2)\mu_1 + X_2\mu_2.$$

Here G_1, G_2 are the weights of the given gas in the mixture, G is the weight of the mixture as a whole, μ_1, μ_2 are the molecular weights of the monatomic and diatomic components, respectively.

Then for the gas constant of the mixture we can write

$$R_\times = \frac{R}{\mu_\times} = \frac{R}{X_2\mu_2 + (1-X_2)\mu_1}.$$

We denote the specific heats at constant volume for the monatomic and diatomic components, respectively, by C_{v1} and C_{v2}. By virtue of additivity, for the specific heats at constant volume and constant pressure of the mixture we have

$$C_v = X_2C_{v_2} + (1-X_2)C_{v_1}, \qquad C_p = C_v + R_\times.$$

The specific heat for the monatomic and the diatomic ideal gases, respectively, will be

$$C_{v_1} = \frac{i}{2}\frac{R}{\mu_1} = \frac{3}{2}\frac{R}{\mu_1}, \quad C_{v_2} = \frac{5}{2}\frac{R}{\mu_2}.$$

Collecting the results obtained, we find the expression for the speed of sound

$$c = \left[gT\left(X_2\frac{5}{2}\frac{R}{\mu_2} + (1-X_2)\frac{3}{2}\frac{R}{\mu_1} + \frac{R}{X_2\mu_2+(1-X_2)\mu_1}\right)\frac{1+3X_2}{1+4X_2}\times\right.$$
$$\left.\times\left(X_2\frac{5}{2}\frac{R}{\mu_2} + (1-X_2)\frac{3}{2}\frac{R}{\mu_1}\right)^{-1}\frac{R}{X_2\mu_2+(1-X_2)\mu_1}\right]^{1/2}.$$

Solving this equation for x_2, from experimental data on the speed of sound we can calculate the volume concentrations of double molecules. For mercury the authors have obtained the expression (neglecting terms with x_2 in degrees higher than the first)

$$X_2 = \frac{18.05 - 2.56c^2/gT}{15.2c^2/gT - 63.15}. \quad (2)$$

Previously, the authors measured the speed of sound in saturated and superheated mercury vapor (with an error of 0.5%) in the temperature range 225–400° C and the pressure range 0.05–2.2 kg/cm². Using these data, volume concentrations have been calculated from Eq. (2) for seven isobars and at the saturation line. The results of the calculation are shown in the table. For each of the isobars the maximum concentration of double molecules is observed at the saturation temperature. With increase in temperature x_2 tends to zero, α tends to unity, and ξ tends to zero. In this case Eq. (1) for the speed of sound assumes the form

$$c = (g(c_p/c_v)R_\times T)^{1/2}.$$

Calculation shows that the least error in x_2, 25% at the isobar, is observed on the saturation line and increases with increase in temperature.

Since the calculation of the concentrations of double molecules from D_0 involves considerable errors, the calculation from acoustic data, which gives an error of 25–50% in the calculations (this error could be substantially reduced by improving the calculation method and increasing the accuracy of the measurements), may be considered satisfactory.

REFERENCES

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