

Pressure Coefficient of Surface Tension and the Expansion Ratio of High Pressure Cloud Chambers*

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IN operating an argon-filled cloud chamber at 110 atmospheres Johnson, De Benedetti, and Shutt¹ found that good tracks were formed with an expansion ratio of 1.04, whereas with the same gas and vapor in a chamber at 1.5 atmospheres tracks were formed with an expansion ratio of 1.07. In both instances the vapor was a 50-50 mixture of water and *n*-propyl alcohol.

A reduction of the expansion ratio with increasing pressure can probably best be understood as an effect of the gas pressure on the surface tension of the droplets. According to the Kelvin theory² of charged droplets, the vapor density δ_r in equilibrium with a droplet of radius r is given by the equation

$$\delta_r = \delta_\infty \exp [(M/R\theta\rho)(2T/r - e^2/8\pi kr^4)], \quad (1)$$

where δ_∞ is the vapor density in equilibrium with a flat surface of the liquid, M is the molecular weight of the liquid, R is the gas constant, θ is the absolute temperature, ρ is the density of the liquid droplet, T is the surface tension, e is the electric charge on the droplet, and k is the dielectric constant of the surrounding gas. Before the expansion, when the temperature is θ_1 and the vapor density is $\delta_\infty(\theta_1)$, ion droplets grow to a radius r_1 where $\delta_{r_1}(\theta_1)$ is equal to $\delta_\infty(\theta_1)$, i.e., $r_1 = (e^2/16\pi kT)^{1/2}$. An adiabatic expansion of the chamber to a volume $(1+\epsilon)$ of the original volume reduces the vapor density to $\delta_\infty(\theta_1)/(1+\epsilon)$ and the temperature to

$$\theta_2 = \theta_1(1+\epsilon)^{1-\gamma}, \quad (2)$$

and the droplet at its lower temperature grows until it is again in equilibrium with the surrounding vapor, a condition expressed by the equation

$$\delta_{r_2}(\theta_2) = \delta_\infty(\theta_1)/(1+\epsilon). \quad (3)$$

Here it is assumed that the time is long enough for the droplet to come into temperature equilibrium with the gas, but so short that no change other than that produced directly by the expansion occurs in the ambient vapor density. The radius of a droplet in equilibrium with the new conditions is found by solving Eq. (1) with the value of δ_r given by (3), and $\delta_\infty(\theta_2)$ equal to the vapor density in equilibrium with a flat surface at the temperature θ_2 of the expanded gas. Here it is convenient to represent the ratio of the saturated vapor densities at the two temperatures by the usual form of equation

$$\ln [\delta_\infty(\theta_1)/\delta_\infty(\theta_2)] = a(1/\theta_2 - 1/\theta_1),$$

and the resulting condition on r_2 may be written

$$2T/r_2 - e^2/8\pi kr_2^4 = (R\rho/M)[a(1 - \theta_2/\theta_1) - \theta_2 \ln(1+\epsilon)]. \quad (4)$$

If the value of r_2 , thus determined, exceeds $r_{\max} = e^2/4\pi kT$ at which δ_r in Eq. (1) has its maximum value, then the droplet can grow indefinitely and reach a visible size. With this value of r_2 inserted in (4) and expressing the

temperatures in terms of the expansion ratio by (2), we find as the condition for the growth of large drops,

$$(1+\epsilon)^{1-\gamma}(a + \theta_1 \ln(1+\epsilon)) = a - (3M/R\rho)(\pi kT^4/2e^2)^{1/2}. \quad (5)$$

The constant a for water has the value 5330, that for *n*-propyl alcohol is 5700, and the constant for the mixture may be assumed to be about 5500. Consequently, the term in θ_1 is negligible, and ϵ is determined by

$$(1+\epsilon)^{1-\gamma} = 1 - (3M/R\rho a)(\pi kT^4/2e^2)^{1/2}. \quad (6)$$

With $M=39$ for the mixture, $\rho=0.9$, $\gamma=1.66$, and $k=1$, Eq. (6) gives values for T of 18.2 and 27.2 dynes per cm corresponding to the observed values 1.04 and 1.07 of $1+\epsilon$ at pressures of 110 and 1.5 atmospheres, respectively. The surface tension of *n*-propyl alcohol is given in the International Critical Tables as 23.8 at normal pressure and 20° C, but no data are given for this liquid when under high inert gas pressures. However, a lowering of surface tension by gas pressure of this order was found for ether and alcohol in atmospheres of air and hydrogen by Kundt.³

The understanding of this effect may lead to a better selection of gas and vapor for high pressure cloud chambers.

* This work was carried out at the Ballistic Research Laboratories, Aberdeen Proving Ground, Maryland.

¹ T. H. Johnson, S. De Benedetti, and R. P. Shutt, *Rev. Sci. Inst.* **14**, 265 (1943).

² Das Gupta and Ghosh, *Rev. Mod. Phys.* **18**, 225 (1946).

³ A. Kundt, *Ann. d. Physik* **12**, 538 (1881).

Anomalous Values of Certain of the Fine Structure Lines in the Ammonia Microwave Spectrum

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RECENT measurements¹ have demonstrated that the fine structure lines in the ammonia microwave spectrum show certain anomalies. The lines arising from transitions between levels where $K=3$ are definitely displaced from the positions predicted for them by the empirical formula which has been constructed to fit the remainder of the lines. The lines arising when transitions occur between levels where $K=3$ and where J is an odd integer are displaced to the long wave-length side of the positions, while those due to transitions between levels where $K=3$ and where J is an even integer are displaced to the short wave-length side.

Qualitatively, the origin of this effect may readily be understood. It is well known that rotation levels where $K \neq 0$ are doubly degenerate. When $K \neq 0$, but is not a multiple of 3, these doubly degenerate levels belong to the mixed symmetry type² $\gamma\delta$ and they cannot be split apart by any perturbation possessing a threefold symmetry, that is, by any perturbation whose origin lies within the ammonia

molecule itself. When $K \neq 0$, and is a multiple of 3, the two originally superimposed levels belong to two symmetry classes^{2,3} α and β . The first of these is symmetric for an interchange of two of the hydrogen nuclei, and the other is antisymmetric for such an interchange. The degeneracy of these levels may be removed by a perturbation which is threefold degenerate. Since the total wave function must be antisymmetric, and since the proton spin functions for three protons possesses no antisymmetric functions, of the two component rotation levels only one can actually occur. The order of the levels is inverted for the excited vibration level giving rise to the microwave spectrum. Thus, the line for $K=3$ will be displaced from its expected position. The direction in which the displacement takes place may be shown to depend upon the oddness or evenness of J .

We have examined the quantum-mechanical Hamiltonian for the ammonia molecule expanded in orders of magnitude and find that a splitting of the levels where $K=3$ occurs in the fourth order of approximation because of an interaction between the first-order Coriolis terms and first-order correction terms to the moments of inertia of the molecule. The constants which are involved are therefore only the usual potential constants together with the dimensions of the molecule and curiously enough do not depend to this approximation upon any anharmonicity in the motion. The displacements may be shown to be of the form

$$\Delta\nu = AF(J), \quad (1)$$

where A is a function of the molecular constants only, and $F(J)$ takes the values $-1, 7, -28, 84, -210$ for values of J from 3 to 7 inclusive. The numerical values may therefore be evaluated with an accuracy which we estimate to be of the order of 10 percent.

In Table I below are given, for various values of J , the

TABLE I. Measured and predicted values of the shifts of $K=3$ lines in the ammonia microwave spectrum.

J	K	Shifts as observed by Good and Coles (megacycles/ second)	Predicted shifts (megacycles/ second)
3	3	-0.30	-0.26
4	3	1.76	1.82
5	3	-7.17	-7.28
6	3	22.3	21.85
7	3	—	-54.62

shifts measured by Good and Coles of lines arising from transitions between levels where $K=3$ together with the values of these shifts predicted by the relation (1).

The displacements where $K=6$ or higher are found to be exceedingly small. A full account of these calculations will appear in the near future.

¹W. E. Good and D. K. Coles, Phys. Rev. 71, 383 (1947); M. W. P. Strandberg, R. Kyhl, T. Wentink, Jr., and R. E. Hilliger, Phys. Rev. 71, 639 (1947). We are also indebted to Dr. Good and Dr. Coles for a private communication giving numerical results which we shall quote in this letter.

²D. M. Dennison, Rev. Mod. Phys. 3, 280 (1931); see especially p. 341. These levels are also said to belong to the symmetry species E. See, for example, G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, New York, 1945), p. 27.

³These levels are also said to belong to the symmetry species A_1 and A_2 , respectively.

Propagation of U. H. F. Sound in Mercury

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MEASUREMENTS have been made of the velocity and attenuation of sound in Hg in the frequency range 100 to 1000 Mc/sec. The electroacoustic transducers used were two identical x-cut quartz crystal disks 0.038 cm thick and 2 cm in diameter. These crystal disks were each cemented on one face across the end of a 50-ohm coaxial line. They were then mounted facing each other in an Hg bath which served simultaneously as: (a) one electrode of each crystal, (b) an acoustic transmission medium, and (c) an electrical shield between the transmitting and receiving crystals.

By means of a micrometer adjustment the separation of the crystals could be varied. In order to obtain separations of the crystals as small as 0.05 cm, which was necessary at the two highest frequencies used, a grid of 0.025-cm diameter silver wires was placed between the crystals to prevent the Hg film from breaking and withdrawing from between the crystals. In addition, in order to insure that the Hg would wet the quartz crystals, the face of each crystal to be immersed in the Hg was coated with an evaporated film of silver before being placed in the bath. These precautions, of course, caused some contamination of the Hg, but the amount (less than 0.1 percent) probably did not affect the measurements.

Conventional transmitters of 50–100 watts power output were used to excite the transmitting crystal through its 50-ohm line, and conventional receivers were used to amplify the output of the receiving crystal. By use of modulated continuous-wave excitation, the band width of the receiving system was held to about 200 cycles/sec. The sound wave was detected by the familiar method of combining the output of the receiving crystal with a direct signal from the transmitter and then changing the separation of the crystals. This change in the separation changed the phase of the acoustic wave incident on the receiving crystal and gave rise to variations in the output of the receiver which approximately repeated as the separation of the crystals was changed by multiples of the acoustic wave-length in Hg. In order to detect sound at the highest frequency used, it was necessary to record the output of the receiver on a recorder driven synchronously with the micrometer controlling the crystal separation.

The attenuation was measured by noting the change in the amplitude of the variations of the receiver output as

TABLE I. Data on propagation of sound in Hg.

Frequency in Mc/sec.	Velocity $\times 10^{-5}$ in cm/sec.	Frequency-free pressure absorption coefficient $\times 10^{17}$ in sec. ² /cm	Temperature °C
0.50 ¹	1.451		20
21.5 ²		6.3	24.3
54.0 ²		6.4	24.3
152	1.449 \pm 0.002	5.8 \pm 0.5	23.8
291	1.451 \pm 0.002	5.5 \pm 0.5	24.0
390	1.450 \pm 0.002	5.7 \pm 0.5	28.2
774	1.47 \pm 0.02	4.7 \pm 1.0	27.2
996	1.44 \pm 0.05	6.0 \pm 1.0	26.9