

# Condensation of vibrationally excited gas

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It is shown theoretically and experimentally that the condensation rate of a gas depends strongly on its vibrational temperature.

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Much attention is being paid of late to nonequilibrium systems of vibrationally excited molecules. These systems are widely used in laser chemistry for controlled stimulation of chemical reactions,<sup>[1]</sup> as active media for gas lasers,<sup>[2]</sup> etc. It should be noted that particular interest attaches here to systems of vibrationally excited molecules at low temperatures of the translational and rotational degrees of freedom. In this communication we consider the condensation of a vibrationally excited gas on the surface of an already-condensed phase<sup>1</sup>.

1. Let a molecule with a reserve of vibrational energy  $\epsilon$  fall into the surface layer of the condensate. In view of the large rate of vibrational relaxation in liquids, it can be assumed that the molecule releases instantaneously its vibrational energy, and this leads to a local heating of the condensate to a certain temperature that varies with time like

$$T(t) = \epsilon / 4c(\pi\chi t)^{3/2}, \quad (1)$$

where  $c$  is the specific heat of the condensate and  $\chi$  is the thermal diffusivity coefficient.

Assuming that the number of particles evaporated per second from 1 cm<sup>2</sup> of surface is given by

$$\nu(T) = n\sqrt{kT/2\pi m} \exp\{-q/kT\}, \quad (2)$$

we find that the quantity

$$W(\epsilon) = (1/a) \int_0^{\infty} \nu(T) dt, \quad (3)$$

( $n$  is the density of the molecules in the condensed phase,  $m$  is the mass of the molecules,  $q$  is the heat of condensation, and  $a$  is the intermolecular distance) characterizes the probability of the molecule becoming condensed or leaving the surface of the condensate: the condition  $W(\epsilon^*) = 1$  determines the minimum reserve of the molecule vibrational energy  $\epsilon^*$ , such that when  $\epsilon > \epsilon^*$  the molecule leaves the surface of the condensed phase.

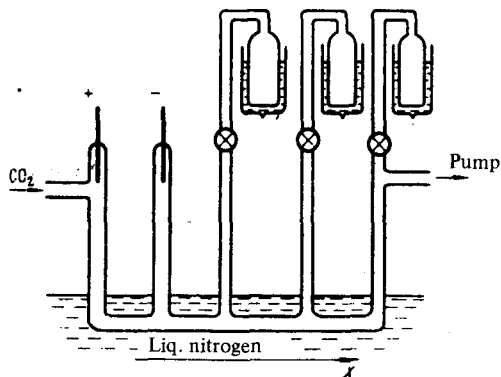


FIG. 1. Experimental setup.

Substituting (1) in (2) and (3) we get

$$\epsilon^* = 10 q^{1/4} m^{1/4} c_0 \rho^{1/2} \chi^{3/2}, \quad (4)$$

where  $c_0 = c/n$  is the specific heat per molecule and  $\rho = mn$  is the specific gravity of the condensate.

Let us estimate  $\epsilon^*$ . We take a gas with a molecular weight  $\sim 100$  and with  $c_0 \sim 10$  cal/deg. Typical values are  $q \sim 1$  kcal/mole,  $\rho \sim 1$  g/cm<sup>3</sup>, and  $\chi \sim 10^{-3}$  cm<sup>2</sup>/sec, so that  $\epsilon^* \approx 1$  eV. The fraction of the molecules that do not become condensed when colliding with the surface is  $\exp(-\epsilon^*/k\Theta)$ , where  $\Theta$  is the vibrational temperature.

The results are valid also for the absorption of vibrationally excited gas. In this case  $q$  should be taken to mean the heat of adsorption, and the parameters  $c_0$ ,  $\rho$ , and  $\chi$  pertain to the adsorbent.

2. The dependence of the rates of condensation on the temperature  $\Theta$  can be verified experimentally by condensing a gas consisting of molecule of two kinds ( $i=1,2$ ) with close vibrational quanta. It is known that of vibrational-vibrational energy exchange in the excitation of the vibrational degrees of freedom these molecules correspond to different vibrational temperatures  $\Theta_i$ , the difference between which is larger the lower the translational temperature of the gas. Depending on the difference between the values of  $\Theta_i$  and  $\epsilon_i^*$ , the condensate will become enriched with molecules of one sort or another.

For an experimental verification it is convenient to choose a mixture of molecules that differ in their values of  $\Theta_i$  but have close values of  $\epsilon^*$ . This conditions is satisfied, for example, by a gas of isotopic molecules. In our experiments we used carbon dioxide, which is a mixture of <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> in a ratio 90:1. Owing to the different vibrational temperatures  $\Theta_i$ , the fraction of uncondensed molecules of different kind will also be different. The ratio of the condensation rates of the isotopic molecules is<sup>[4]</sup>

$$\exp[(\nu_i - \nu_j) / \nu_i^* (\epsilon^* / T_0)], \quad (5)$$

where  $\nu_i$  is the frequency of the vibrational quantum of the molecule of kind  $i$  and  $T_0$  is the translational tem-

perature of the gas.

According to (5), the rate of condensation (adsorption) of molecules containing the lighter isotope turns out to be larger.

3. The experiment was performed with the setup illustrated in Fig. 1. Carbon dioxide was pumped through a cell placed in liquid nitrogen. The pumping rate was  $\sim (2-3) \times 10^3$  cm/sec, and the gas pressure was  $\sim 1$  Torr. A glow discharge was maintained in the first section of the cell. The vibrationally excited CO<sub>2</sub> molecules produced in the discharge were then frozen out in the second, third, and fourth sections. It follows from the foregoing results that the first to be frozen out are the lighter molecules, and consequently the concentration of the molecules containing <sup>13</sup>C should increase with increasing distance from the discharge. Previously evacuated bulbs were connected to taps from the second, third, and fourth sections.

The gas was pumped through the cell for several minutes. The supply of gas was then interrupted and the discharge was turned on. The sampling bulbs, immersed in the liquid nitrogen, were then connected to the working cell. While the condensate was slowly and simultaneously thawed out, the gas condensed in a different section was refrozen in the corresponding bulbs. To avoid strong mixing, a small amount of gas was drawn.

The gas frozen in the bulbs was analyzed with an SP-8 mass spectrometer. The measurement results are shown in Fig. 2. The peaks of  $I_{44}$  and  $I_{45}$  correspond to the molecules <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>3</sub>, respectively. From a comparison of the obtained mass spectra with the mass spectra of natural CO<sub>2</sub> it follows that the peaks  $I_{28}$  and  $I_{29}$  are determined mainly by the molecules <sup>12</sup>CO and <sup>13</sup>CO, which are produced in the discharge as a result of the reaction  $2\text{CO}_2 = 2\text{CO} + \text{O}_2$ . Since this reaction requires a noticeable activation energy, the CO molecules become enriched with <sup>13</sup>C in comparison with the CO<sub>2</sub> molecules.<sup>[5]</sup> A noticeable increase of the content of <sup>13</sup>C with increasing distance from the discharge is noted for both the CO<sub>2</sub> and the CO molecules.

In the experiment, the vibrationally excited gas was pumped over the condensate, and the region in which

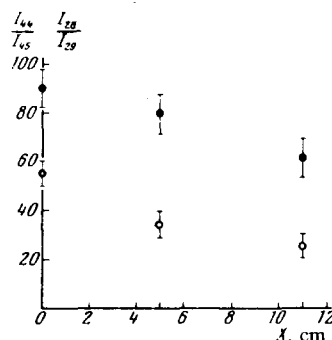


FIG. 2. Dependence of the molecule isotopic ratio of the length of the freezing zone: a—<sup>12</sup>CO<sub>2</sub>/<sup>13</sup>CO<sub>2</sub> (dark circles); b—<sup>12</sup>CO/<sup>13</sup>CO (light circles).

the molecules collided with the surface of the condensate was quite large. In addition, drawing the samples from the surface of the condensate was inevitably accompanied by partial mixing of the molecules evaporated from different regions of the surface. Finally, when a molecule with a reserve of vibrational energy falls on the surface, its evaporation is accompanied by evaporation of a certain number of already condensed molecules. All these circumstances should make the dependence of the isotopic composition of the condensate on the length of the freezing zone worse than that expected from the developed theory. Therefore, a noticeable difference in the properties of the isotopic molecules, which was observed in our experiments, indicates that the effective energy  $\epsilon^*$  is quite large.

For comparison, we have frozen-out  $\text{CO}_2$  molecules without exciting the gas with a discharge. Analysis of the samples for the isotopic composition gave the same results, corresponding to the natural isotope ratio, for the samples from different sections of the apparatus.

1) The first indication that the rate of condensation of the gas depends on the vibrational energy of the molecules is contained in<sup>[3]</sup>.

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