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The formation of gas bubbles in supersaturated fuel is considered. A formula is obtained for the critical bubble radius.

We report the results of an investigation into the influence of various materials on the nature of liberation of gas from a fuel. We examine the condition under which bubbles form in the fuel and gas escapes not only through the surface separating the fuel and gas layer but also through the surface of the growing bubbles as well.

Supersaturation of a solution is easily eliminated [1] by the introduction of solid particles or gas bubbles, or by contact with rough surfaces.

Dean [2] analyzing the data of several authors on bubble formation, and the results of his own experiments on the state of gases from water, concluded that the problem of liberation of gas bubbles from a liquid supersaturated by a gas is completely analogous to the problem of bubble formation in a superheated fluid. He concluded that water supersaturated by gas will not form bubbles provided there are no gas bubbles at dust particles or other solid inclusions and the water is not subjected to mechanical shaking.

Glaser [3] found that a superheated fluid will boil under radioactive irradiation. An important result was the detection of the radiation sensitivity of supersaturated solutions of gases in liquids [4]. It was shown in [5] that charged particles initiate nucleation bubbles in a liquid, with size reaching about  $10^{-6}$  cm.

As a rule, fuel tanks contain a large number of structural materials with varying surface roughnesses. In this connection, the initiating effect was investigated for several grades of rubber, and bronze, brass, and stainless steel chips in vacuum evaporation of fuel. The tested rubbers were distributed as follows in order of increasing initiating capability: type 203B sheet rubber, 3826 sheet rubber, and vacuum rubber. Bubble formation began at an absolute pressure of  $0.6-0.7 \text{ kg/cm}^2$ . In a pure glass vessel, no liberation of air bubbles was observed even at  $0.01 \text{ kg/cm}^2$ . Severe shaking did not result in bubble formation.

An experimental investigation was also made of the initiating effect of model panels of aluminum alloys and stainless steel with spot-welded angle pieces. The release of gas in the form of bubbles was observed to begin at  $0.55 \text{ kg/cm}^2$  near the joints and at the spot welds. No liberation was observed from the remaining surfaces up to a pressure of  $0.05 \text{ kg/cm}^2$ . At  $0.15 \text{ kg/cm}^2$ , bubbles were liberated for 4 h; after this time, the gas content was cut by half. Bubble formation was observed at the same points on the surfaces. The number of formation centers depended on the roughness of the materials and the presence of cracks. In a repeated test of materials held for a certain time in partially degassed fuel, the initiating effect was found to be weaker, and sometimes entirely absent. After air drying, the materials regained their ability to initiate the evolution of gas.

These data indicate that the basic factor responsible for the release of air bubbles from the fuel is the presence of nucleation bubbles of air in dense, microcracks, and pores of the investigated material. It should be noted that the initiating effect of materials is unstable, since air bubbles remaining on the surface of materials in contact with the fuel may change in size owing to diffusion exchange with the fuel. The following processes were observed in the experiment. If vacuum evaporation was carried out immediately after the rubber specimen was dropped into the fuel, evolution of gas in the form of bubbles was observed

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Fig. 1. Forms of bubble nuclei: a) at wetted wall; b) at unwetted wall.

at 0.45 kg/cm<sup>2</sup>. When the rubber was first held in fuel for 30 min at atmospheric pressure, evolution was observed at  $0.12 \text{ kg/cm}^2$ .

In vacuum-evaporation of fuel in the presence of a steel angle piece covered with a layer of rust, the rate of evolution dropped sharply, depending on the holding time before commencement of vacuum treatment. This indicates that owing to the good wettability of the test materials by T-6 fuel and to fuel surface tension, even at atmospheric pressure there is dissolution of air bubbles remaining on the surface after immersion of the specimen in fuel saturated with air at this same pressure.

In all bubbles having a convex surface, the gas pressure is greater than  $P_{bar}$  by an amount  $\gamma_l = 2\sigma/r$ . Thus if the fuel is saturated with air at  $P_{bar}$ , the bubbles may dissolve in time. Let us look at the condition for dissolution of bubbles that can serve as initiators of separation of gas from the fuel in vacuumevaporation of the fuel saturated with air at  $P_{bar}$  after it has been poured into the tank and stored at atmospheric pressure. The gas pressure in a spherical bubble is

$$P_{\rm g} = P_{\rm bar} + \gamma_l h + \frac{2\sigma}{r} - P_s. \tag{1}$$

The equilibrium pressure of gas over a concave bubble surface is less than the equilibrium pressure over the flat surface,  $P_i$ , and in accordance with the Kelvin law is

$$P_{\rm ib} = P_i - \sigma \left(\frac{1}{r_1} + \frac{1}{r_2}\right) \frac{\gamma_{\rm g}}{\gamma_{\rm l} - \gamma_{\rm g}} \,. \tag{2}$$

For fuel saturated at the partial gas pressure  $P_{\text{bar}}$ , the condition for dissolution of a spherical gas bubble is represented by the inequality

$$P_{\rm g} > P_{\rm bar} - \frac{2\sigma}{r} \frac{\gamma_{\rm g}}{\gamma_{\rm l} - \gamma_{\rm g}} \,. \tag{3}$$

Substituting  $P_g$  into this expression, we obtain

$$P_{s} < \frac{2\sigma}{r} \left( 1 - \frac{\gamma_{g}}{\gamma_{l} - \gamma_{g}} \right) + \gamma_{l} h, \qquad (4)$$

which is the condition of bubble annihilation for the above conditions. Bubble dissolution takes place by diffusion owing to the difference in gas concentration in the fuel and the equilibrium concentration corresponding to the gas pressure in the bubble.

When vessels are filled, microcracks, scratches, and microirregularities in metal walls, rubber pores, synthetic materials, glass, etc., may remain unfilled with liquid. The air or other gas remaining will initiate release of gas in the form of bubbles at the vessel walls when a particular radius is reached; it depends on the shape and size of the defect from which the bubbles grow, the properties of the gas and liquid, and the pressure. Suspended particles carrying bubble nuclei also facilitate the release of gas as bubbles.

Depending on wettability, the nucleation bubbles at the walls will be concave or convex. Figure 1 shows the possible types of nucleus.

Let us look at the condition for bubble equilibrium in the liquid, and the expression for the critical radius of a bubble located at a wettable surface.

The equilibrium equation can be written as

$$P_s + P_{\rm ib} = P_{\infty} + \gamma_l h + \sigma \left(\frac{1}{r_1} + \frac{1}{r_2}\right). \tag{5}$$

After substitution of  $P_{ib}$  and  $P_i$ , found from the Henry law, the equilibrium condition (5) for a bubble of gas in a liquid with a gas concentration  $A_i$  in the liquid takes the form

$$P_s + \frac{A_i}{k_{ii}} = P_{\infty} + \gamma_l h + \sigma \left(\frac{1}{r_1} + \frac{1}{r_2}\right) \left(1 + \frac{\gamma_{gi}}{\gamma_l - \gamma_{gi}}\right), \tag{6}$$

while when there are k gases dissolved in the liquid,

$$P_{s} + \sum_{i=1}^{k} \frac{A_{i}}{k_{ii}} = P_{\infty} + \gamma_{l} h + \sigma \left(\frac{1}{r_{1}} + \frac{1}{r_{2}}\right) \left(1 + \sum_{i=1}^{k} \frac{\gamma_{gi}}{\gamma_{l} - \gamma_{gi}}\right).$$
(7)

The term  $\sum_{i=1}^{k} \gamma_{gi}/(\gamma_{l}-\gamma_{gi})$  can usually be neglected, since it is ordinarily small as compared with unity.

Using the expression obtained, it is easy to determine the critical radius of a nucleus for the known gas concentrations in liquids or, conversely, the critical concentrations when the nucleus dimensions are known.

For example, for a nucleus with spherical surface convex toward the liquid,

$$r_{\rm cr} = \frac{2\sigma}{\sum_{i=1}^{k} \frac{A_i}{k_{ii}} + P_s - P_{\infty} - \gamma_l h}$$
(8)

Bubbles with radii less than the critical value will dissolve, while those with greater than critical radius will grow. Only bubbles with radius equaling  $r_{cr}$  will be in unstable equilibrium. In approximation, our example reflects the case in which the nuclei are located at a wettable surface.

If the surface cannot be wetted by the liquid, the bubble equilibrium condition takes the form

$$P_s + \sum_{i=1}^{\kappa} \frac{A_i}{k_{ii}} = P_{\infty} + \gamma_t h - \frac{2\sigma}{|r|} , \qquad (9)$$

while the bubble growth condition is

$$P_{s} + \sum_{i=1}^{k} \frac{A_{i}}{k_{ii}} > P_{\infty} + \gamma_{\rm L} h - \frac{2\sigma}{|r|} .$$
 (10)

If

$$P_s + \sum_{i=1}^{n} \frac{A_i}{k_{ii}} \leqslant P_{\infty} + \gamma_{\rm L} h,$$

the bubbles can grow to a certain size, whereupon growth ceases. For unwettable walls, therefore, the condition for stable release of gas as bubbles will be

$$P_s + \sum_{i=1}^k \frac{A_i}{k_{ti}} > P_{\infty} + \gamma_l h.$$
<sup>(11)</sup>

Thus for  $\sum_{i=1}^{n} A_i/k_{ti} = 0$  we obtain the conditions for boiling of liquids containing no dissolved gas.

The formula obtained for the critical bubble radius can be used to evaluate the influence of changes in the conditions on separation of gases.

As an example, let us look at the results of an experiment with T-6 fuel, saturated with nitrogen at  $3 \text{ kg/cm}^2$ .

In these experiments, we found far more centers of separation than in vacuum evaporation of the fuel. The cause becomes obvious when we use the proposed critical-radius formula. For a fuel saturated at  $3 \text{ kg/cm}^2$ , as the pressure drops to  $1 \text{ kg/cm}^2$ , the critical radius becomes roughly half that for vacuum evaporation of ordinary fuel saturated at  $1 \text{ kg/cm}^2$ , down to an absolute pressure of  $0.05 \text{ kg/cm}^2$ . Thus in the first case more small bubbles are capable of growing owing to the diffusion of dissolved gas in them.

There are contradictory opinions as to the influence of mixing on separation of a dissolved gas from a liquid. Some authors [2] state that vortices form during mixing, and tensile forces appear at the center of the vortices, resulting in separation of the liquid and formation of a nucleus, which can continue to grow if the solution is supersaturated.

In our opinion, some of the vortices must generate nuclei whose radii exceed the critical value for the given conditions, if mixing or agitation of liquid flowing through pipes is to lead to separation of gas as bubbles. If a vortex generates nuclei with radii below the critical value, they will dissolve. In general, some of the nuclei with the below-critical radii can combine if they enter the zone of a new vortex and, merging, exceed the critical radius. In addition, vortex formation can lead to local pressure drops near nuclei existing at walls and particles, where the radii are below the critical value for the average flow conditions. At the pressure prevailing in the vortex zone, the radius may prove above the critical value, and the nuclei will begin to increase in size, continuing to do so as long as the vortex exists. As a result, the radius of the nucleus may exceed the critical value for the average flow conditions, and the bubble will initiate separation of gas from the flow.

## NOTATION

$\gamma_l$ , $\gamma_g$	are the specific gravity of liquid and gas;
σ	is the surface tension of the liquid;
r, r <sub>1</sub> , r <sub>2</sub>	are the radii of curvature of the surface;
Ai	is the concentration of gas in liquid;
A <sub>ti</sub>	is the gas solubility coefficient;
P <sub>bar</sub>	is the barometric pressure;
P <sub>bub</sub>	is the pressure within the bubble;
$P_s$	is the saturated vapor pressure;
$P_g$	is the pressure of the gas within the bubble;
$\mathbf{P}_{l}^{\mathbf{O}}$	is the pressure within the liquid surrounding the bubble;
Pi	is the partial pressure of the gas that corresponds to equilibrium between liquid and gas for a
	plane phase interface;
$P_{ib}$	is the equilibrium pressure of the gas in the bubble;
P	is the pressure above the surface of the liquid.

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