COOLING OF A VOLATILE LIQUID THROUGH WHICH A GAS IS BUBBLED

B. N. Yudaev, O. V. Tsirlin,
and A. A. Yushkin

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A method is proposed for calculating the temperature in the two-phase system consisting of a volatile liquid through which a gas is being bubbled. Some results are given for the water–air system.

Bubbling, or the passage of a gas through a liquid, is widely used in heat- and mass-transfer processes in many branches of industry (the chemical, petrochemical, and food industries, for example). When a gas is injected into a liquid, the liquid evaporates within the gas bubbles and is consequently cooled. This method is convenient for use e.g., in cooling liquid hydrogen and liquid oxygen. As the bubbles rise through the liquid, surface-active substances are adsorbed at the gas–liquid interface and then carried to the liquid surface. Bubbling devices could thus be used instead of expensive cooling towers to cool and purify waste water. Similar processes are involved in artificial hearts and lungs, in which blood is saturated with oxygen. The mass- and heat-transfer processes accompanying bubbling are thus of considerable interest.

We consider a system (Fig. 1) consisting of a liquid and a gas moving in a vertical vessel which is subjected to an external heat flux. We are to determine the temperature of the liquid leaving the vessel. The gas bubbles formed at the nozzles move at velocities $U_\infty \sim 25$ cm/sec with respect to the liquid [1-3]; the bubbles reach these steady-state velocities after a time $t_1 \sim 10^{-5}$ sec [2]. We thus know the time t_2 the bubble spends in the vessel if we know the liquid level and the liquid flow rate; in typical devices this time is orders of magnitude larger than t_1. Heat and mass transfer between a single gas bubble and a liquid have been studied previously, e.g., in [1, 4, 5]. The characteristic time t_3 for these processes in the case of volatile liquids is some 10^{-3}-10^{-2} sec, which is again orders of magnitude smaller than the typical values of t_2. It follows from these comparisons that in estimating the efficiency of the cooling system we

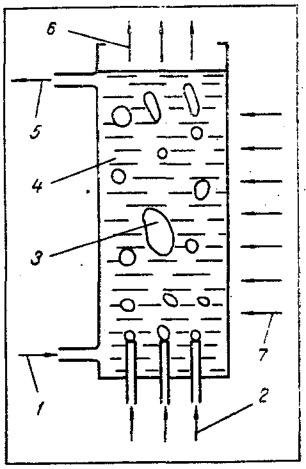

Fig. 1. Diagram of the cooling process. 1) Inlet for the liquid, component A, and the gas dissolved in it, component B, at molar flow rates of $\dot{n}_{Ai}$ and $\dot{n}'_B$, enthalpies h''_{Ai} and h''_{Bi}, respectively; 2) inlet for the gas, component B, and the vapor of component A carried with it, at molar flow rates of $\dot{n}_B$ and $\dot{n}''_{Ai}$ and enthalpies h''_{Bi} and h''_{Ai}, respectively; 3) gas of composition X''; 4) liquid of composition X'; 5) drain for liquid A and the gas B dissolved in it; 6) drain for gas B and the vapor A carried with it; 7) external heat flux q_a.

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can begin from the assumption that a thermodynamic phase equilibrium is reached instantaneously; i.e., we can assume that each parameter involved in the process has the same value at all points in the working volume.

We also assume that the liquid and gas flow rates are constant and that the cooling is isobaric and reversible; we expect temperature changes over narrow ranges (some tens of degrees), so that the specific heats of the components as well as the latent heats of vaporization and dissolution (of the gas in the liquid) are constant, independent of the temperature; and we assume the external heat flux q_a (Fig. 1) to be constant and specified. Some investigators (e.g., Bykov [6]) emphasize that the gas bubbles cause extensive mixing of the liquid as they rise; the external heat flux is thus essentially equivalent to a set of heat sources distributed uniformly throughout the liquid.

The continuity equations for the two components are

$$\dot{n}'_A = \dot{n}'_{Ai} - \dot{n}''_A, \tag{1}$$

$$\dot{n}'_B = \dot{n}_B - \dot{n}''_B. \tag{2}$$

For an isobaric process the first law of thermodynamics yields

$$q'_A + q'_B = q'_{Ai} + q''_{Bi} + q''_{Ai} - q''_A - q''_B + q_a. \tag{3}$$

We rewrite this equation in parametric form,

$$T\left(1 + \frac{1}{PG}\right) = \frac{\Phi}{P}\left[PI + B + J + H - \frac{\dot{n}''_A}{\dot{n}_B} + F\left(1 - \frac{\dot{n}''_B}{\dot{n}_B}\right) + \frac{q_a}{c'_A \dot{n}_{Ai}}\right], \tag{4}$$

and then in dimensionless form:

$$(\Theta + A_1)\left(1 - \frac{1}{PG}\right) = \frac{A}{P}\left[PI + B + J + H - \frac{\dot{n}''_A}{\dot{n}_B} + F\left(1 - \frac{\dot{n}''_B}{\dot{n}_B}\right)\right] + E, \tag{5}$$

where $\Theta = T - T_B / T_A - T_B$ is the dimensionless temperature, T_A and T_B are the saturation temperatures for components A and B, and we use the groups of parameters

$$P = \frac{\dot{n}_{Ai}}{\dot{n}_B}; \quad G = \frac{C'_A}{C''_B}; \quad I = \frac{h_{Ai}}{h_{fqA}}; \quad B = \frac{h_{Bi}}{h_{fqA}};$$

$$J = \left(\frac{\dot{n}''_{Ai}}{\dot{n}_B}\right)\left(\frac{h''_{Ai}}{h_{fgA}}\right); \quad H = \left(\frac{\dot{n}'_{Bi}}{\dot{n}_B}\right)\left(\frac{h'_{Bi}}{h_{fgA}}\right); \quad F = \frac{h_{fgB}}{h_{fgA}};$$

$$\Phi = \frac{h_{fgA}}{C'_A}; \quad A = \frac{1}{T_A - T_B}\left(\frac{h_{fqA}}{C'_A}\right); \quad A_1 = \frac{T_B}{T_A - T_B};$$

$$E = \frac{1}{T_A - T_B} \cdot \frac{q_a}{C'_A \dot{n}_{Ai}}.$$

In Eq. (5), which is our basic equation for calculating the properties of the cooling process, we assume that we know the initial values of I, B, P, G, F, J, H, and E. We must keep in mind that the ratios of the vapor flow rate $\dot{n}''_A$ and the gas flow rate $\dot{n}''_B$ out of the vessel to the gas flow rate at the inlet, $\dot{n}_B$, are functions of the temperature. The particular functional dependences are governed by the $x' = \varphi_1(T)$ and $x'' = \varphi_2(T)$ phase-equilibrium curves, which we assume to be known.

We introduce the notation

$$\frac{n'_B}{n'_A} = X' = \frac{1 - x'}{x'} = f_1(\Theta), \tag{6}$$

$$\frac{n''_B}{n''_A} = X'' = \frac{1 - x''}{x''} = f_2(\Theta), \tag{7}$$

where the mole fraction of component A in the gas phase is

$$x'' = \frac{p_s}{p_a}, \tag{8}$$

p_s is the saturation vapor pressure of component A, p_a is the external pressure, and x' is the mole fraction of component A in the liquid phase.

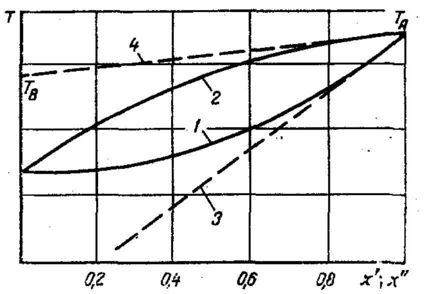

Fig. 2. Typical phase-equilibrium diagram for components A and B. 1) Boiling curve; 2) condensation; 3) line used to approximate the boiling curve, $x' = 1 - \varepsilon(1-\Theta)$; 4) line used to approximate the condensation curve, $x'' = \Theta$. Here x' is the mole fraction of component A in the liquid phase, and x'' is the same in the gas phase.

Differentiating (6) and (7) with respect to the time and using (2), we find

$$\frac{\dot{n}'_A}{\dot{n}_B} X' + \frac{n'_A}{\dot{n}_B} \dot{X}' + \frac{\dot{n}''_B}{\dot{n}_B} = 1; \tag{9}$$

$$\frac{\dot{n}''_A}{\dot{n}''_B} = \frac{1}{X''} - \frac{\dot{X}''}{X''^2} \cdot \frac{n''_B}{\dot{n}''_B}. \tag{10}$$

We assumed above that the phase equilibrium is reached essentially instantaneously, so that there is no subsequent exchange of mass between the rising bubbles and the surrounding liquid: $\dot{X}' = \dot{X}'' = 0$.

The gas in the liquid reduces the overall specific heat of the system; using the equation at the end of the previous paragraph along with Eq. (1), we find from (9) and (10) that

$$\frac{\dot{n}''_B}{\dot{n}_B} = 1 - \dot{X}'P + \frac{X'}{X''}, \tag{11}$$

$$\frac{\dot{n}''_A}{\dot{n}_B} = \frac{1}{X''} - \frac{X'}{X''} P - \frac{X'}{X''^2}. \tag{12}$$

Substituting (11) and (12) into (5) and solving the resulting equation, we find the temperatures of the liquid and the gas in the vessel.

If the cooling is slight, i.e., if the temperature change of the liquid is slight (some tens of degrees), we can replace this part of the phase-equilibrium curve by a straight line segment. In particular, near the saturation point $T = T_A$ (Fig. 2) we could write

$$x'' = \Theta, \tag{13}$$

$$x' = 1 - \varepsilon(1 - \Theta), \tag{14}$$

where $\varepsilon = (\partial x'/\partial\Theta)_p$ is the slope of the boiling curve. Substituting (13) and (14) into (11) and (12) and then substituting the result into (5), we find an equation for Θ:

$$a_0\Theta^3 + a_1\Theta^2 + a_2\Theta + a_3 = 0, \tag{15}$$

where

$$a_0 = \varepsilon\left(1 + \frac{1}{PG}\right); \tag{16}$$

$$a_1 = \left(1 + \frac{1}{PG}\right)[1 - \varepsilon(2 - A_1)] - \frac{A}{P}\varepsilon(2 + P) + \frac{\varepsilon FA}{P}(1 + P) - \varepsilon\left[\frac{A}{P}(PI + B + J + H) + E\right]; \tag{17}$$

$$a_2 = \left(1 + \frac{1}{PG}\right)[A_1 - 1 + \varepsilon(1 - 2A_1)] - \frac{A}{P}[1 - \varepsilon(1 + P)] - \frac{\varepsilon FA}{P}(1 + 2P) + (2\varepsilon - 1)\left[\frac{A}{P}(PI + B + J + H) + E\right]; \tag{18}$$

$$a_3 = \varepsilon FA - \left(1 + \frac{1}{PG}\right)(1 - \varepsilon) A_1 + \left[\frac{A}{P}(PI + B + J + H) + E\right](1 - \varepsilon). \tag{19}$$

If, in this case of slight cooling, the initial liquid temperature differs significantly from the saturation temperature, then the linear approximation of the phase-equilibrium curve leads to an equation for Θ which is of the same form as (15), except that Eqs. (13) and (14) and thus the equations for the coefficients a_0, a_1, a_2, and a_3 are slightly different.

In the particular case in which the gas is insoluble in the liquid or the latent heat of dissolution is negligible in comparison with the latent heat of vaporization, we would have $F = 0$; then instead of Eq. (15) we would have the following equation for Θ:

$$a_1\Theta^2 + a_2\Theta + a_3 = 0, \tag{20}$$

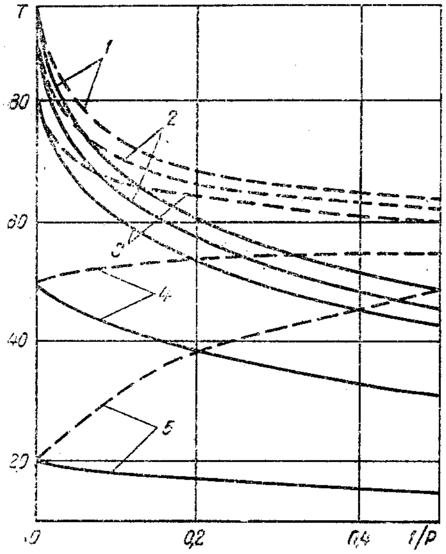

Fig. 3

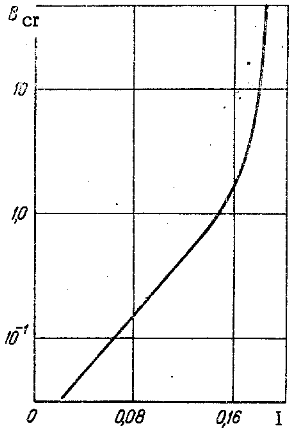

Fig. 4

Fig. 3. Water temperature as a function of the relative air flow rate. 1) T_{Ai} = 99°C; 2) 90; 3) 80; 4) 50; 5) 20. The solid curves are for T_{Bi} = 20°C, and the dashed curves are for T_{Bi} = 400°C.

Fig. 4. Critical value of the parameter B as a function of the relative enthalpy of the liquid at the inlet for the water—air system.

where the coefficients are found from (16)-(19) for $\varepsilon = 0$. The solution of (20) is

$$\Theta = \frac{-a_2 - \sqrt{a_2^2 - 4a_1a_3}}{2a_1}. \tag{21}$$

The sign of the radical was chosen on the basis of physical considerations. For example, with a zero gas flow rate and zero external heat flux, the value of Θ should remain equal to its initial value Θ_i, as it does if we choose the minus sign; the plus sign corresponds to $\Theta = 1$, which cannot hold.

Let us examine solution (21). Depending on the ratio of the liquid and gas enthalpies at the inlet, the liquid can be either cooled or heated. It is clear from physical considerations that the ratio of the component flow rates should not determine whether it is cooling or heating which occurs, so in determining the dependence of the degree of cooling on the parameter 1/P we assume that the heat added to the system by the gas is negligible; i.e., we set $I = (\Theta_i + A_1)/A$, $1/G = 0$ and $B = 0$ in Eqs. (16)-(19). Then from (21) we find

$$\Theta = \frac{1 + \Theta_i + \frac{A}{P}(J + 1)}{2} - \sqrt{\frac{\left[1 + \Theta_i + \frac{A}{P}(J + 1)\right]^2}{4} - \Theta_i - \frac{A}{P}J}. \tag{22}$$

We see from this equation that as the gas flow rate is increased, i.e., as 1/P increases under otherwise fixed conditions, the value of Θ decreases. If the gas and liquid temperatures at the inlet are the same, we can substitute the parameter J into Eq. (22) in the form

$$J = \frac{\Theta_i (h_{Ai} + h_{fgA})}{(1 - \Theta_i) h_{fgA}}.$$

We thus find that if the gas is already saturated vapor at the inlet there is no change in the temperature of the liquid; i.e., $\Theta = \Theta_i$. Obviously, we want to minimize J (maximize the initial dryness of the gas). If these temperatures are approximately equal to each other and to the saturation temperature of the liquid, then the injected bubbles turn out to be centers of vapor formation. Under such conditions the cooling is most efficient (a formal analysis of (22) shows that Θ should tend toward zero, but the liquid can be near the saturation temperature only if heat is continuously supplied from without). The cooling is of course intensified as the latent heat of vaporization increases: as $A \to \infty$, the dimensionless temperature Θ tends toward zero.

We are particularly interested in determining the initial values of the parameters corresponding to the most efficient cooling. We can evaluate this efficiency on the basis of the degree of cooling, i.e., the difference between the initial and final values of Θ:

$$\Theta_i - \Theta = \frac{\Theta_i - 1 - \frac{A}{P}(J+1)}{2} + \sqrt{\left[\frac{\Theta_i - 1}{2} + \frac{A}{2P}(J+1)\right]^2 + \frac{A}{P}}$$

$$= \frac{\frac{A}{P}[1 + (\Theta_i - 1)(1 + J)]}{\frac{1-\Theta_i}{2} + \frac{A}{2P}(J+1) + \sqrt{\left[\frac{1-\Theta_i}{2} - \frac{A}{2P}(J+1)\right]^2 + \frac{A}{P}}}. \tag{23}$$

We conclude from this latter equation that the cooling ($\Theta_i - \Theta$) becomes more pronounced as the temperature of the liquid at the inlet rises. Accordingly, the maximum temperature drop for a fixed ratio of flow rates, 1/P, is reached when the liquid is near the saturation temperature.

The parameter B is a measure of the enthalpy of the gas at the inlet; when B is large, the liquid becomes heated, since the amount of heat added by the gas is larger than the amount of heat expanded on vaporization. The critical (in this sense) values $B_{cr} = B(I)$ are governed by

$$\Theta_i - \Theta = 0. \tag{24}$$

From this equation, which states that the temperature of the liquid at the drain does not differ from the initial temperature of the liquid, we find an equation for the critical values of B:

$$B_{cr} = \frac{I}{G} + \frac{IA - A_1}{1 - (IA - A_1)}. \tag{25}$$

It should be noted that the parameter I varies in proportion to the dimensionless temperature (it is a linear function of this temperature).

The parameter G is equal to the ratio of the molar specific heat of the liquid to that of the gas; for most gases and liquids the specific heats are weak functions of the temperature. In our problem they are determined from the initial temperatures. Clearly, if the gas which is injected is cooler than the liquid, it would be preferable to use a gas having a large specific heat; in the opposite case, a gas having a small specific heat should be used.

In general, the dissolution of the gas in the liquid is accompanied by the evolution of heat, so that the cooling will be less pronounced if the gas has a relatively low solubility. This point should be carefully considered in cryogenic applications of this cooling method. For example, gaseous helium (not gaseous nitrogen, which is more soluble) should be used to cool liquid oxygen or liquid hydrogen by bubbling.

It is also interesting to note how the degree of cooling depends on the shape of the phase-equilibrium curve. Where we can use the linear approximation of this curve and where we can neglect the effects of the absolute values of the saturation temperatures of the components, this dependence is characterized by the slope of the curve, $k = (\partial T_s / \partial x'')_p$, where T_s is the saturation temperature for the given value of x''. To write the degree of cooling, $\Delta T = T_i - T$, as a function of k, we set $E = B = J = H = F = 0$ in (5) and write the solution of this equation as

$$\Delta T = T_i - \frac{T_B + T_i + k + \frac{h_{fgA}}{PC'_A}}{2} \pm \frac{\sqrt{\left[T_B + T_i + k + \frac{h_{fgA}}{PC'_A}\right]^2 - 4\left(T_B \frac{h_{fgA}}{PC'_A} - kT_i + T_B T_i\right)}}{2}. \tag{26}$$

It follows that as k increases ($k \to \infty$) $\Delta T \to T_i$ and $T \to 0$; i.e., a pronounced cooling is achieved through the use of liquids having relatively steep phase-equilibrium diagrams. As the saturation temperature increases, the degree of cooling becomes larger and larger, approaching a maximum as the critical state is approached.

If the cooling of the liquid is very pronounced, it is better to reproduce large parts of, or even the entire, equilibrium curve in a common analytic form. The basic difficulty involved here is that the gas saturation temperature can be found from the available experimental data only approximately, by extrapolating the curve to the point at which the amount of vapor of the liquid in the gas is assumed to vanish. In particular, for the water–air system this state corresponds to a temperature $T_B = -60°C$. Then the equilibrium curve is described by

$$x'' = \Theta^5. \qquad (27)$$

This dependence gives a good description of the phase equilibrium for any external pressure. Using (27) and neglecting the quantities ε and F (air dissolves poorly in water and has a low latent heat of dissolution), we find the following equation for the temperature of the water–air system:

$$a_1\Theta^6 + a_2\Theta^5 - a_1\Theta + a_3 = 0, \qquad (28)$$

where the coefficients a_1, a_2, and a_3 are again found from (16)-(19). Figure 3 shows a solution found numerically for Eq. (28); as 1/P increases, the temperature decreases. There is evidently a value of I such that the final temperature of the liquid is higher than its initial temperature. The cooling is more intense at low ratios of the gas flow rate to the liquid flow rate than at large values of this ratio. If the object of the process is not so much to achieve a large temperature drop as it is to remove heat at a high liquid flow rate, or at a large throughput, it is best to use small values of the parameter 1/P. The refined data confirm the qualitative conclusion reached on the basis of the simplified equilibrium curve. For example, for given values of 1/P and B, the cooling becomes more pronounced as the temperature of the liquid at the inlet increases.

Numerical methods have led to quite accurate calculations of the theoretical values of B_{cr}. To determine them, we replace Θ in (28) by Θ_i; we then find (25). Figure 4 shows the $B_{cr} = B_{cr}$ (I) dependence. As expected, at values of I corresponding to the saturation temperature, the final temperature of the liquid differs little from its initial temperature, even if the temperature of the gas at the inlet is very high.

This method for calculating the temperature in cooling systems based on bubbling can be extended to any pairs of components and to mixtures.

NOTATION

n	is the number of moles of the given component, kmoles;
$\dot{n}$	is the molar flow rate, kmoles/sec;
q	is the heat supplied per unit time to the system, kJ/sec;
T	is the temperature, °C;
C	is the partial molar specific heat, kJ/(kmole · deg);
h	is the partial molar enthalpy, kJ/kmole;
h_{fgA}	is the partial molar latent heat of vaporization, kJ/kmole;
h_{fgB}	is the partial molar latent heat of dissolution, kJ/kmole;
X	is the ratio of mole fractions;
x	is the mole fraction of component A;
p	is the pressure, N/m^2;
$\varepsilon = (\partial x'/\partial \theta)_p$	is the slope of the boiling curve;
$k = (\partial T_s/\partial x'')_p$	is the slope of the condensation curve.

Subscripts

a	is the surrounding medium;
A	is the component A;
B	is the component B;
i	is the inlet conditions;
s	is the saturation line;
''	is the gas phase;
'	is the liquid phase.

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