# The Wave of Water-Ice Phase Transition as the "Burning" Wave

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## **1** Introduction

It is well known from general physics (for example, [1]), that under certain conditions water can be in a state of unstable equilibrium, referred to as the supercooled liquid (Fig.1, curve LB). Under shockwave influence on nucleation centers in such medium, a phase transition from liquid to crystalline state is realized. Such processes can be observed, for example, as an aircraft icing at its flying through a cloud of supercooled water vapor in the top atmospheric layers. Analogous situation can be realized and for superheated steam (curve GA on Fig.1), when it condensates from gaseous phase to liquid vapor (for example, [2]).



Fig.1. Typical isotherms of van der Waals gas.

The process of the phase transition of water-ice is accompanied with energy release and can be considered as an example of a system with positive energy release, typical for combustion and detonation processes in reactive mixture. If the column of the supercooled liquid is imagined as analog of long cylindrical explosive charge, the condensation waves can propagate along such charge, excited, for example, by the shock-wave effect on the butt-end (Fig. 2).



Fig.2. 1 - supercooled water, 2 - ice, 3 - the front of condensation wave.

Such condensation wave is analogous to usual combustion waves propagating along a charge of combustible mixture.

### **2** The Assumptions

The propagation of the condensation wave can be analyzed on base of the conservation laws of mass, momentum and energy (equations 1-3), used at description of propagation of combustion and detonation waves in the reaction mixture (in the system of the wave front for any two planes of the stream tube of constant cross section):

$$\rho_0 v_0 = \rho v$$

$$P_0 + \rho_0 v_0^2 = P + \rho v^2$$

$$H_0 + v_0^2 / 2 = H + v^2 / 2 + Q$$
(1-3)

where  $v_0$  and v – flow velocity (in and out relative to the front) in the selected sections,  $\rho$  – density, P – pressure, H – enthalpy, Q – specific energy release of mixture [3]. For algebraic manipulation with equations system (1-3) the analytical form of the function H = U + PV (and also U as the internal energy) is required. The analytical form of H = U + PV (and also U) is the most important question

for individual phase state at widest range of pressure-temperature-density variation: ideal or real gas, liquid or solid, different heterogeneous system... Unfortunately, the functions U = U(S, V) and H = H(S,P) are well known in the form of tabulated tables (for example, [4-7]) and in analytical form only for some specific systems (such as ideal gas, photonic gas,...), here *S* is the entropy. Polynomial form of the global thermodynamic potential of U(S,V), H(S,P), F = U - TS = U(T,V) and G = F + PV = U - TS + PV = G(T,P) is not optimal for algebraic manipulation with equations system (1-3), so different approximated formula for thermodynamic potentials are widely used at estimations.

After selection of analytical form of H(S,P) the additional relation S=S(P,V) is need for function H = H(P,V). Then at known parameters of the initial state  $(\rho_0, P_0, H_0(\rho_0, P_0))$  the additional equation needs for determination of the unknown parameters  $(v_0, \rho, v, P, H(P,V), Q)$  – the equation among P and V for given system and given process. Such equation is named as the thermal state equation of the medium. For water the Tait equation (4) [8] is used most often:

$$P/P_0 = B[(\rho/\rho_0)^{7.15} - 1].$$
(4)

For clarity of mathematical transformation this equation is usually presented in the form of (5)

$$P = A\rho^n, (5)$$

so an enthalpy can be expressed as an additional ratio (formula (6))

$$H = \frac{n}{n-1} \frac{P}{\rho}.$$
 (6)

The first two equations for a fixed wave velocity  $v_0$  lead to equation of the line in the (P, V) – plane, it is called the Michelson-Rayleigh line (7) (MR-line) –

$$\frac{P - P_0}{V - V_0} = -\rho_0^2 v_0^2 \,. \tag{7}$$

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For clarity, it is usually assumed that Q = const n = const, then the energy equation (3) after the transformation (taking into account (6)) can be rewrite as the functional relation  $P_Q = F(V,Q)$ , called the energy adiabatic curve (8) – EAC:

$$\left(\frac{P}{P_0} + \frac{n-1}{n+1}\right)\left(\frac{V}{V_0} - \frac{n-1}{n+1}\right) = 1 - \left(\frac{n-1}{n+1}\right)^2 + 2\frac{n-1}{n+1}\frac{Q}{P_0V_0}$$
(8)

When Q = 0, we obtain the equation of the shock adiabatic curve  $P_{SW} = F(V)$ .

Energy adiabatic curve  $P_Q$  is a hyperbole, shifted with respect to a point on the initial state so that the point O lies outside the hyperbola (Fig. 3). Energy adiabatic curve  $P_Q$  (line 1 in Figure 3) consists of a supersonic detonation branch (in the quadrant to the left and above the O) and subsonic deflagration branch (in the quadrant to the right and below the point O). From O to this hyperbole can spend a lot of lines. There are three variants of the relative position of the adiabatic energy curve  $P_Q$  and an individual line: a) there is no intersection, b) the intersection is in the two points, and c) single contact of MR-line and EAC.

From the initial point the two tangents can be leaded, one would characterize the minimum speed of supersonic detonation (point D) (9),

$$D_D \approx \sqrt{2(n^2 - 1)Q} \tag{9}$$

second (point F) – maximum speed of subsonic combustion (10)

$$D_{df} = nP_0 / \rho_0 D_D . \tag{10}$$

Ratios (9) and (10) are obtained from the simultaneous solution of equations (7) and (8) in the above case b) - search for points of contact. For gas mixtures when  $n \equiv \gamma = c_P / c_V$  the last relation gives

$$D_{df}D_D = c_0^2$$

( $c_P$  and  $c_V$  - specific heat capacities,  $c_0$  - sound speed).

State of the mixture without reaction is characterized by the shock adiabatic curve  $P_{SW}$  (line 2 in Figure 3).



Fig.3. Typical diagram of fuel-air mixture and its products on (PV)-plane (pressure - specific volume).

Let us consider the subsonic branch of EAC  $P_Q = F(V,Q)$ . Conservation laws satisfy any flame spread – from the low-speed mode of the normal burning (defined by processes of heat conduction and diffusion) to a maximum velocity of turbulent combustion (determined by the condition of tangency to the lower branch – deflagration EAC). From a mathematical point of view the normal burning is determined from the solution of equation of unsteady heat conduction for a system with energy release

$$c_P \rho \frac{\partial T}{\partial t} = div(\lambda \cdot gradT - c_P \rho u_n T) + q$$

 $\lambda$  – thermal conductivity,  $u_n$  - flow velocity (for static the flow velocity equals to the velocity of normal burning), q – the specific (per unit volume) of the energy flux density of the thermal source at a time. The law of energy release of the mixture at the combustion process represents the most important element at solving of this equation, determined by the laws of chemical kinetics. Laminar flame with a minimum speed corresponds to a state close to the point P = const, the maximum speed deflagration (touching point F) corresponds to the high turbulent combustion. The task about ratio among the velocity of normal burning and the maximal velocity of deflagration (as turbulent burning) is unsolved up to now. For example, for most mixtures of gaseous hydrocarbon fuels with air the velocity of the normal burning amounts to approximately 0.3 m/s and the maximum speed of deflagration – about 60 m/s (ratio about 200). For hydrogen-air mixtures the diffusion coefficient is much higher, and the velocity of burning has another values: about 3 m/s for laminar flames and 70 m/s for turbulent burning. Note that the turbulent flame speed is determined by the condition of tangency to subsonic branch of EAC P<sub>Q</sub> = F(V,Q) and its value is determined with sufficient accuracy, as opposed to the velocity of normal burning.

## 3 "Heat Transfer" Estimation

From 1–D (plane) task about the water freezing in contact with the frosty air, formed ice thickness x versus time t is given by

$$x = \sqrt{\frac{2\lambda \cdot \Delta T \cdot t}{\rho q}}$$

where  $\lambda$  is the thermal conductivity coefficient of an ice,  $\rho$  – density of an ice, q – specific melting heat of an ice,  $\Delta T$  - temperature difference between the ice and the air. For example, at 10–degree frost an ice thickness will be equals  $\approx 11.3$  cm/day ([1], page 175), which gives the average speed of the condensation front V<sub>cf</sub>  $\approx 1,3$  10<sup>-6</sup> m/s, which is many orders of magnitude less than the speed of thermal motion of the molecules of H<sub>2</sub>O.

## 4 Estimation of the Condensation Wave as of "the Combustion Wave"

At  $Q = 80 \text{ cal/g} \approx 3.4 \ 10^5 \text{ m}^2/\text{s}^2$  [9] and n = 7.15 the velocity of "Detonation"  $D_D \approx 5800$  m/s and the maximum velocity of deflagration  $D_{df} \approx 0.12$  m/s can be obtained easily from (9) and (10) (sound speed in water  $c_0 = 1500$  m/s). Such deflagration velocity is fixed easily by human eye. One can see that the "wave" estimation predicts the velocity of condensation front exceeds by many orders of "heat transfer" assessment.

Since  $D_{df}$  is the maximum speed in range of the normal (laminar) to turbulent flames, so the value  $D_{df} \approx 12$  cm/s represent the upper limit of the velocity of condensation front. The actual speed of the condensation front must be similar to the "normal burning". As noted above, for gaseous mixtures contained hydrogen atoms, the ratio between turbulent and laminar flame velocities is about 20 - 200. It is impossible to obtain an estimate of this ratio for heterogeneous medium with a phase transition due to an absence of correct theory of nucleation and its development.

If the value 20 to be proposed as the ratio for homogeneous mixtures, the lower estimate of the velocity of condensation front should be at the level of 0.006 m/s (6 mm/s).

Thus, using the analogy of the energy at the phase transition as the chemical energy that provides propagation of combustion and detonation waves in a gas mixture, the estimation for the velocity of crystallization front can be proposed –  $V_{cf} = 12 - 0.6$  cm/s. Experimental velocity of condensation front is a few (2 – 4) centimeters per second, which should be recognized as the good agreement with the proposed assessment. Similar experiments were conducted with supercooled water in glass test-tube, the start of condensation process in tube was initiated by small droplet of usual water, impinged on the upper surface of supercooled water.

## 5 Conclusion

If the condensation wave in the supercooled liquid considered as an analogue of normal burning wave propagating in the charge of the combustible mixture, the velocity of condensation front is predicted in order of centimeters per second, typical for velocity of "laminar flame".

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