

$$(dP/dT)_\lambda = -(P_{\lambda 2} - P_{\lambda 1}) / (T_{\lambda 1} - T_{\lambda 2}) \approx -100 \text{ at/deg.}$$

2) An important factor is that the theory contains a temperature-independent characteristic dimension $(a_0^2 a_\lambda)^{1/3} \approx 1.1 \times 10^{-3} \text{ cm}$. It is implied throughout that the transverse dimensions of the vessel are much larger than all the three characteristic dimensions a_0 , a_λ , and $(a_0^2 a_\lambda)^{1/3}$ of the theory.

3) We note the interesting equation
$$\int_0^{x_0} f^2 dx = \left(\frac{df}{dx} \right)_{h_s}^2 - \left(\frac{df}{dx} \right)_{-h_n}^2.$$

INTENSIFICATION OF A SHOCK WAVE BY THE POLYMERIZATION ENERGY AND THE FEASIBILITY OF A POLYMERIZATION DETONATION

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The polymerization of several solid monomers by a shock wave was recently observed [1]. Thus, for example, it was noted that passage of a shock wave with amplitude of 50 kbar or higher causes 60% of acryl amide to be converted into a polymer. It is known [2] that the polymerization energy of acryl amide is about 10 - 15 kcal/mole. Thus, the energy released in 60% polymerization of acryl amide is $E_p = 10 \text{ kcal/mole}$. It is of interest to compare this quantity with the energy E_s obtained by the substance as a result of compression by the shock wave. The change in the internal energy of one gram of matter compressed by a shock wave, without allowance for the energy of the chemical processes, is equal to $E_s = P(V_0 - V)/2$, where V_0 is the specific volume of the substance prior to compression, and V is the specific volume of the substance compressed to a pressure P . To obtain the dependence of the specific volume of the substance on the applied pressure it is necessary to determine the shock adiabat of the investigated substance.

To determine these quantities in acryl amide we use the values obtained for Plexiglas and polystyrene, which have the same initial density and approximately equal compression coefficients. We assume that the shock adiabat for the acryl amide differs little from the shock adiabats of Plexiglas [3] and polystyrene [4], which are very close to each other at $P < 100 \text{ kbar}$. Then at a pressure $P = 5 \times 10^{10} \text{ dyne/cm}^2$ the relative compression is $V/V_0 = 0.74$. From this we get $E_s \approx 10 \text{ kcal/mole}$ for acryl amide with $V_0 = 0.85 \text{ cm}^3/\text{g}$. As is well known [4], at pressures lower than $10^{11} \text{ dyne/cm}^2$ the thermal component of the internal energy of the compressed substance does not exceed half the total energy. Therefore heating of the substance by the shock wave amounts to approximately 200°C . On the other hand, the shock of polymerization (assuming that it occurs during the passage of the shock wave) heats the substance by 400°C ¹⁾. The total temperature rise of the compressed substance is therefore not less than 600°C .

If the resultant mixture of monomer and polymer were to be cooled by thermal conductivi-

ty - a sufficiently slow process - then after passage of the rarefaction wave the temperature of the substance should greatly exceed the melting temperature. Yet the authors have observed that after passage of the shock wave the substance shows no traces of melting. This is evidence of its exceedingly rapid adiabatic cooling to $t < 100^{\circ}\text{C}$ (the melting point of acryl amide at normal pressure). From this we can conclude that a considerable portion of the thermal energy released at the instant of polymerization is transferred to the shock wave, being converted into elastic energy of the substance. As can be seen from the foregoing arguments, the energy released during polymerization is approximately equal to the energy lost by the shock wave to the compression of the monomer. Therefore the additional fraction of the energy obtained by the shock wave from the chemical processes is comparable with the total energy obtained by the substance upon compression by the shock wave.

According to Yu. B. Khariton [5,6], in order for detonation to occur it is necessary that the time of chemical reaction of the shock-wave-compressed substance be shorter than the time of lateral scattering.

Recently N. M. Kuznetsov carried out, at the authors' request, a detailed theoretical analysis [7] and showed (with phase transformation as an example) that the condition that the chemical transformation be exothermal is neither sufficient nor necessary for realization of detonation: the detonation can occur if the specific volume of the substance increases under isobaric and isenthalpic transition.

This raises the question whether a detonation process can occur as a result of polymerization by a shock wave. When a solid monomer becomes polymerized the specific volume of the polymer reaction product is usually somewhat smaller than the specific volume of the initial substance ²⁾. Because the shock compression was applied to a polycrystalline monomer compressed at high pressure ($\rho_0 \approx 1.18$), the effective density of the resultant polymer hardly differed from the effective density of the initial substance. At a pressure on the order of 50 kbar the specific volume of the compressed monomer, as indicated above, is $V = 0.74$ with $V_0 = 0.62 \text{ cm}^3/\text{g}$. This is much lower than the specific volume of the polymer ($V \approx 1.1 \text{ cm}^3/\text{g}$) under ordinary conditions, so that the pressure relaxation behind the front of the wave prevails over the contraction connected with the polymerization, and the substance expands. Therefore the pressure of the polymerization products will exceed the pressure of the initial substance and the condition for the occurrence of a detonation process in Kuznetsov's form will be satisfied. The energy released upon polymerization is approximately one order of magnitude lower than the calorie content of the solid explosives, and the temperature in the wave front will, as indicated above, be low. However, since the activation energy of the polymerization in the shock wave is very small [1], the reaction can proceed rapidly and at sufficiently low temperatures. Therefore the reaction rate may be sufficiently large to make the critical detonation dimension realistically attainable.

Thus, the experimentally observed intensification of a shock wave by the polymerization energy and Kuznetsov's theoretical data make the feasibility of polymerization detonation a valid question.

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1) We assume here that the specific heat of the monomer and of the polymer is $C = 0.3$ cal/g and neglect the change of specific heat with pressure.

2) In the case of detonation of a fulminating mixture the specific volume of the water-vapor reaction products is also smaller than the volume of the initial substances.

ERRATA

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On p. 201 lines 26-27 instead of $V = 0.74$ with $V_0 = 0.62 \text{ cm}^3/\text{g}$ read $V = 0.74V_0 = 0.62 \text{ cm}^3/\text{g}$.