CRUCIAL PRESSURE INDEX FOR NITROGLYCERINE SENSITIVITY

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INTRODUCTION

The vapor pressure of nitroglycerine can be varied by applying a relatively moderate hydrostatic pressure at a constant temperature. In an ideal and oversimplified approximation, the vapor pressure is shown to approach one value that is designated here as a crucial pressure. The existence of any such pressure implies an enhanced volatility. With increased volatility, vaporization steps that are affected can be so fast that even a high-velocity detonation can be supported in the vapor phase.

Although such results are only qualititative, the implication that vapor pressures are profoundly affected by hydrostatic pressures is verified by both theory and experiment (ref. 1,2). This role of hydrostatic pressures in the explosive decomposition of propellants and explosives has not been considered.

BACKGROUND DISCUSSION

The increased volatility of a condensed phase under hydrostatic pressure was noted as early as 1881 (ref. 1). This effect has been studied and confirmed by many investigators, and a survey of the subject is available (ref. 2). The effects of hydrostatic pressure are generally described as the sum of two independent factors, namely, enhancement of the vapor pressure of the condensed phase and effects of intermolecular forces between gas-vapor molecules. The phenomena are comparable to osmosis in which solution pressures greater than that of the pure solvent are generated and maintained in an equilibrium situation. An illustration of the scheme is given in Figure 1.

For the purpose of this paper, the effect of intermolecular forces can be ignored. The enhancement of the vapor pressure can then be evaluated directly by equating the chemical potential changes of the liquid and the vapor, respectively, which are influenced by the hydrostatic pressure, π. Thus, at constant temperature, T,

$$\Delta G_L = \int_P^{\pi} V_L \, dP = \Delta G_g = \int_{P^\circ}^{P} f(P) \, dP \qquad (1)$$

where G and V are molal free energies and volumes, respectively, P is the pressure, f(P) is an appropriate equation of state, the subscripts L and g refer to the liquid and vapor, respectively, and the superscript ° refers to the pure system.

The liquid is generally assumed to be impermeable to, and incompressible by, the pressurizing medium since these restructions allow the direct evaluation of the first integral. A fair approximation to the second integral is obtained by a virial equation for the vapor of the form RT/P + B, where B is the second virial coefficient (ref. 3). The results of both integrations are equated and rearranged in the following form:

$$P + P^{\circ} e^{\frac{V\pi}{RT} + \frac{B\ P}{RT} + \frac{P^{\circ}(V + B)}{RT}} \qquad (2)$$

This equation relates the vapor pressure of a condensed phase in a manner that is independent of intermolecular forces. It suggests as a first approximation the exponential dependency of the vapor pressure with the external pressure.

From the standpoint of chemical kinetics the rates of vaporization and condensation must be equal at equilibrium. Condensation rates are proportional to the pressure and a maximum rate is predicted from the kinetic theory (ref. 3) as

$$\dot{n} = 1/(2\ \pi\ M\ RT)^{-1/2}\ P \qquad (3)$$

where $\dot{n}$ is the collision frequency in moles per unit area per unit time. Hence, the maximum rate of vaporization is predicted by Equation 3, and, subject to some oversimplification, the enhanced vapor pressure of Equation 2 leads to an enhanced vaporization rate.

APPLICATION

The purpose of this paper is simply to call attention to the significance of the fact that the vapor pressure of a liquid can be affected by the application of a hydrostatic pressure at a constant temperature. Explosive sensitivity and initiation are usually interpreted on the basis of at least two mechanisms that may or may not be independent, namely, vaporization and reaction. In the case of a compound for which vaporization is a rate-controlling step (i.e., by a required supply of reactant to support the reaction in the vapor phase), it seems likely that a theoretical index to explosive sensitivity can be based on a defined ease of volatility.

Equation 2 predicts the manner in which the vapor pressure of a liquid can increase with the application of a hydrostatic pressure. Under the restrictions that

$$B = 0 \quad \text{and} \quad V\pi \gg P^{\circ}\ (V + B)$$

(i.e., an ideal gas) a condition is indicated in which the new vapor pressure of the liquid can in principle approach the value of the

applied hydrostatic pressure. Although it is obvious that such an interpretation of the state of affairs is limited, it is informative to calculate such variations in the vapor pressure up to the limiting pressure, which is designated here as a crucial pressure for a material such as nitroglycerine. These values of the vapor pressure are converted to maximum volatilities by the kinetic theory approximation of Equation 3.

DISCUSSION

Several simplifications that have been introduced make the results listed in Table 1 appear quite inapplicable to the real situation. However, the implications of such an analysis persist, namely, that an increased volatility of nitroglycerine at constant temperature can occur by the application of a hydrostatic pressure.

Table 1 shows that quite moderate pressure will increase the volatility to rates near detonation. The product of molecular density and low and high-velocity detonation rates (approximately 2000 and 8000 m/sec (ref. 4), respectively) give estimates of specific consumption rates of 1410 and 5640 moles/cm^2-sec, respectively. Pressures of less than 4 kilobars can generate such vaporization rates. For comparison, the pressures that exist in propagating shock fronts are in the range of 5 to 100 kilobars (ref. 5); the value of 40 kilobars has been quoted for nitroglycerine (ref. 6). With such pressures available it does seem desirable to introduce the concept of a crucial pressure, since the ease of volatility has been enhanced so much that it is unnecessary to consider vaporization as a rate-limiting step in the process. Thus, this effect can act in a cascade fashion -- where increased pressure causes faster reactant supply by vaporization, exothermic reaction causes more pressure (because of temperature rises and generally more product moles per reactant mole), ad infinitum.

The crucial pressure, when calculated with an appropriate approximation can be an index to the explosive sensitivity of a material when the initiation process is rate-controlled by vaporization.

Of course, it should be recognized that it is not the pressure alone that is crucial, since the causes of this effect are the intermolecular forces that are involved in solutions. For example, although recent results (ref. 7) report a hundredfold increase in the vapor pressure of napthalene in argon for a hydrostatic pressure of only 200 bars at 22°C, but a twofold decrease is reported for a comparable situation in helium.

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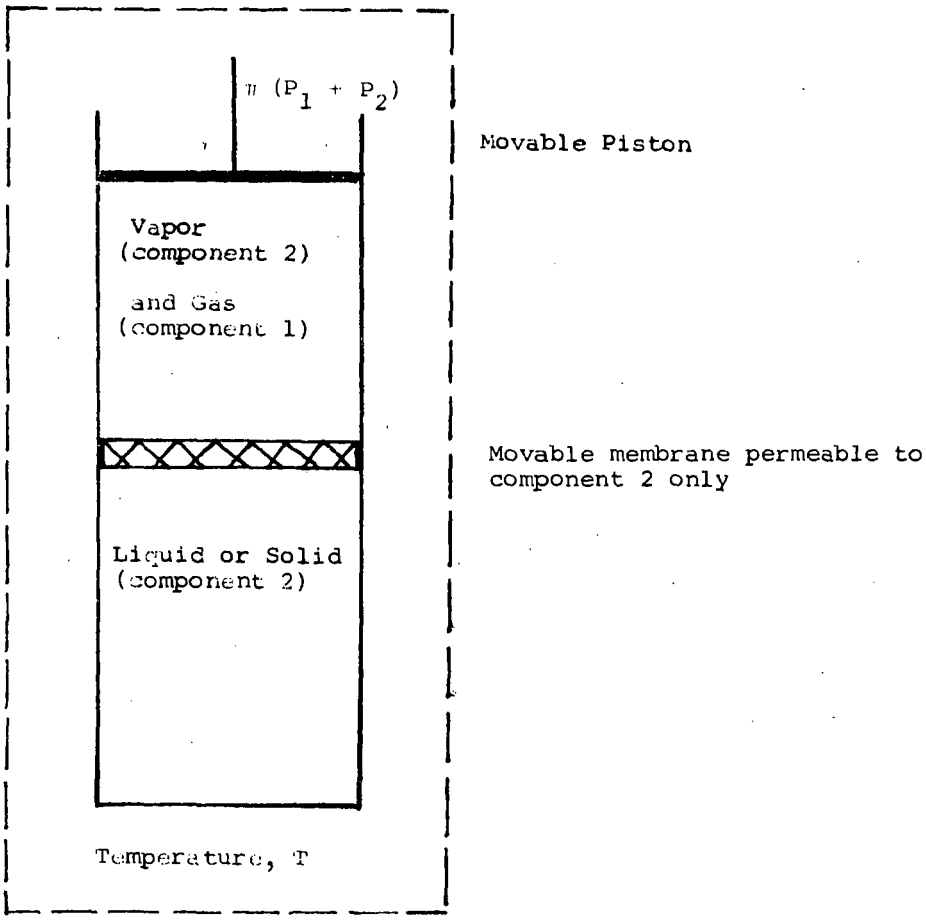

Figure 1

SCHEME OF THE HYDROSTATIC PRESSURE EFFECT

Table 1

HYDROSTATIC PRESSURE EFFECTS ON NITROGLYCERINE

Hydrostatic Pressure, π, bars	Vapor Pressure of Nitroglycerine, bars	Vaporization rate, moles/cm^2-sec
0	0.00000068	0.000000115
68	0.00000100	0.000000169
341	0.00000494	0.000000839
680	0.0000347	0.00000588
1020	0.000248	0.0000420
1360	0.00166	0.000282
1730	0.015	0.00254
3470	330	55.8
3610	806	1410*
3850	2980	5640*
3920	3920	---

*Vaporization rate required to maintain consumption rate of low- and high-velocity detonations, 2000 and 8000 m/sec, respectively (ref. 4) in nitroglycerine.

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