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On Entropy and Free Energy of Explosives (preliminary communication)

by

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Summary. An attempt is made to explain some experimental facts related to explosives in terms of the entropy and hence of the free energy of explosives. A discussion is given on the change with temperature of the sensitivity to impact and on the rate of detonation of two-phase explosives.

The reference is given now to the work of Urbański and Sikorska [1] on the change of sensitivity of TNT to impact with temperature. A pertinent fact is a noncontinuous trend of the curve with a bend at the melting point of the substance (curve *I*, Fig. 1). Curve *I* strikingly resembles that of the change of free energy ($G = H\text{-}ST$) with temperature and the bend at the melting point—curve *G* [2].

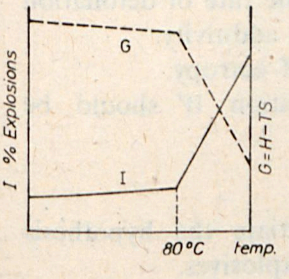

Fig. 1. Sensitivity of TNT to impact (curve *I*) and free energy (curve *G*) against temperature

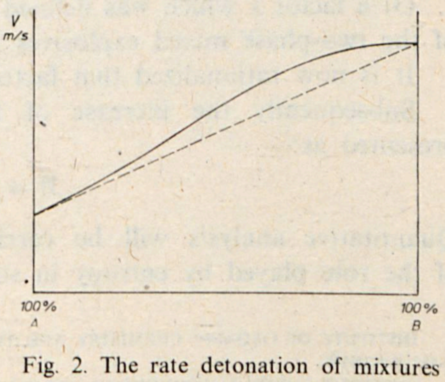

Fig. 2. The rate detonation of mixtures of two solid explosives

It is now rationalized that the trend of curve *I* is due to the increase of entropy with temperature including a rapid increase with melting.

Another problem crops out from the rate of detonation of the mixtures which according to my previous work [3] and that of Laffitte and Parisot [4] deviate from the additivity towards higher values (Fig. 2). It is known that the entropy of mixtures is higher than that of individual components. This experimental finding is now rationalized in terms of a relatively high entropy and lower free energy of two solid phase system.

I have also found that the rate of detonation of a mixture of equimolar quantities of mono- and trinitrotoluene is higher than that of dinitroluene under the same experimental conditions (the same confinement, density and the charge diameter) [5]. This is shown in Fig. 3.

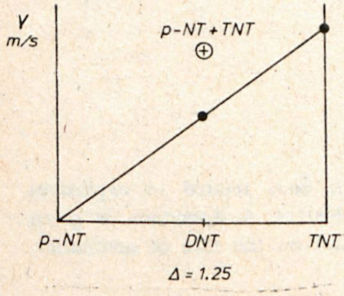

Fig. 3. The rate of detonation of 2,4-dinitrotoluene (DNT) and of the equimolar mixture MNT+TNT(*p*-nitrotoluene+α-trinitrotoluene)

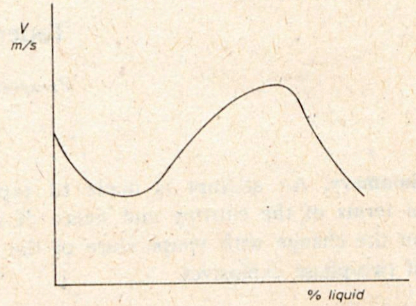

Fig. 4. The rate of detonation of solid explosives (TNT, PETN, Hexogen) with nonexplosive liquids

In the experiments carried out in [5] and [6] the influence was shown of adding nonexplosive liquids to solid explosives. The phenomenon is a complicated function of several factors. This was rationalized as a function of:

(1) the change of "covolume" α (from the van der Waals equation),

(2) "phlegmatizing" (desentizing) action φ of the liquid,

(3) a factor x which was defined as an increase of the rate of detonation of the two-phase mixed explosives in comparison with additivity.

It is now rationalized that factor x is a function of entropy.

Subsequently the increase of the rate of detonation W should be presented as:

$$W = f(\alpha, \varphi, S).$$

Quantitative analysis will be carried out to substantiate the hypothesis of the role played by entropy in some properties of explosives.

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REFERENCES

[1] T. Urbański, A. Sikorska, Bull. Ac. Pol.: Chim., **6**, 617 (1958).

[2] A. R. Ubbelohde, *Melting and crystal structure*, Clarendon Press, Oxford, 1965.

[3] T. Urbański, Przemysł Chem., **22**, 521 (1938); Mém. artill. franc., **20**, 237 (1946); *Chemistry and technology of explosives*, vol. III, Pergamon Press–PWN, Oxford–Warsaw. 1967, pp. 250–251.

[4] P. Laffitte, A. Parisot, Compt. rend., **203**, 1516 (1936).

[5] T. Urbański, Archives of Combustion Processes, **3**, 117 (1972).

[6] T. Urbański, T. Galas, Compt. rend., **209**, 558 (1939).

Т. Урбаньски, **Об энтропии и свободной энергии взрывчатых веществ (предварительное сообщение)**

Работа представляет попытку выяснения некоторых экспериментальных явлений касающихся взрывчатых веществ из точки зрения энтропии и свободной энергии этих соединений. Обсуждено изменение чувствительности к удару под влиянием температуры, а также скорость детонации двухфазных взрывчатых веществ.