On the Equation of State for Gases at Extremely High Pressure

P. Caldirola

of Eq. (13) to the free energy of activation and the absolute rate of reaction. Unfortunately, the perturbation method is considerably complicated by the essential degeneracy of many of the benzenoid vibrations. Since for the cases under consideration the two benzene rings are identically substituted, every vibration of the diphenyl molecule is at least doubly degenerate and those corresponding to the doubly degenerate levels of the benzene ring are fourfold degenerate. In principle, these degeneracies can be eliminated, and the perturbation method can be carried through to completion. However, since the steps necessary to this solution are concerned with the details of the particular example chosen, it seems best to postpone the presentation of the explicit solution of this case. The authors hope soon to carry out numerical calculations based on this development.

IV

Although the present treatment has been restricted to a consideration of the racemization of diphenyls, it is clearly of much broader application. An equation analogous to (12) will predict the energy of reaction for those cases in which an equilibrium constant rather than a rate constant can be observed.

V

The authors wish to thank Dr. G. W. Wheland for his valuable advice and assistance in this research.

On the Equation of State for Gases at Extremely High Pressure

P. CALDIROLA
Istituto di Fisica, Università di Pavia, Pavia, Italy
(Received July 18, 1946)

On the basis of the thermo-hydrodynamic theory of the explosive detonation—developed by Chapman, Jouguet, and R. Becker—a procedure is developed permitting the deduction of the equation of state for gaseous mixtures from explosive processes. The equation is established by starting from several sets of experimental data. In this way one can semi-empirically derive the equation of state for gases compressed up to 10^4–10^5 atmos. The results of numerical calculations are reported.

1

DIRECT experimental measurements allow one to derive the equation of state for gases up to pressures of some thousand atmospheres. But we have little knowledge about the properties of gases compressed up to 10^4–10^5 atmos.; this is the order of the instantaneous pressures of gaseous products resulting from the detonation of solid explosives. Therefore, the fundamental importance, from the chemical-physical viewpoint, presented by the knowledge of the properties of gases at these particular conditions is evident.

The purpose of this work is in the first place to show that, when one admits the validity of the thermo-hydrodynamic theory of detonation

as developed by Chapman,[1] Jouguet,[2] and R. Becker,[3] and makes use of a few experimental data, then one can determine the equation of state for gases applicable during the detonation: the pressures of these gases can be of the order of 10^5 atmos.
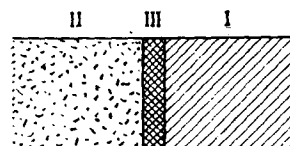
In order to make more comprehensible our

FIG. 1. Explosion process.

---

[1] D. L. Chapman, Phil. Mag. **47**, 90 (1899).
[2] Jouguet, J. de Math. **1**, 347 (1905); **2**, 6 (1906).
[3] R. Becker, Zeits. f. Physik **8**, 321 (1922).

procedure, we will sketch briefly the thermo-hydrodynamic theory of the explosion. Let us consider, for this purpose, Fig. 1, which represents, at a certain instant, the state of the system composed of the unexploded substance, and the products obtained in the detonation, when the explosive reaction takes place in a cylindrical container with indeformable walls. The part of the container on the right I is filled with the unexploded substance (gas, liquid, or solid), the part on the left II is filled by the mixture of the explosion products, and the intermediate part III represents the zone (whose depth, following Becker, is about 10^{-7} cm), where the explosive transformation takes place. Let us denote by D the velocity with which this zone (wave front) proceeds (velocity of detonation), and W the velocity of the gaseous explosion products; let us denote by ρ_1, T_1, p_1 and by ρ, T, p the density, the temperature, the pressure, respectively, of the unexploded substance and of the gaseous products.

In the steady conditions ($D=$const.), and assuming that the effect of heat losses is negligible, the principles of continuity of mass, conservation of energy, and momentum, then, provide the following equations:

$$\rho_1 D = \rho(D-W), \qquad (1)$$

$$p_1 D + \rho_1 D\left(E_1 + \frac{D^2}{2}\right)$$
$$= p(D-W) + \rho(D-W)\left[E + \frac{(D-W)^2}{2}\right], \quad (2)$$

$$p_1 + \rho_1 D^2 = p + \rho(D-W)^2 \qquad (3)$$

(E_1 and E denote the specific internal energy of two phases).

To the preceding equations, which are hydrodynamical in nature, we shall now add the thermodynamic relation:

$$E - E_1 = \int_{Tt}^{T} c_v dT - q = \bar{c}_v(T - T_1) - q, \qquad (4)$$

and the equation of state for the gases of the mixture resulting from explosion:

$$F(\rho, p, T) = 0. \qquad (5)$$

It can easily be shown that Eqs. (1)–(5) permit one to obtain D, W, T as functions of the

parameters p, ρ and of the characteristics of the unexploded substance:

$$D = \left[\frac{p - p_1}{\rho - \rho_1}\frac{\rho}{\rho_1}\right]^{\frac{1}{2}}, \qquad (6)$$

$$W = \left[(p - p_1)\frac{\rho - \rho_1}{\rho\rho_1}\right]^{\frac{1}{2}}, \qquad (7)$$

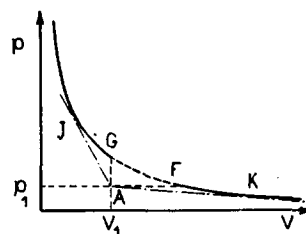$$T = \varphi(\rho, p). \qquad (8)$$

FIG. 2. Hugoniot's curve for an explosion process.

Moreover, one arrives at a relation between p and v (where $v = 1/\rho$ is the specific volume of the gaseous mixture):

$$\bar{c}_v[\varphi(p, v) - T_1] - q = \tfrac{1}{2}(p_1 + p)(v_1 - v). \quad (9)$$

This relation is represented on the (V, p) diagram (Fig. 2) by a curve known as Hugoniot's curve or H curve. This gives us all the infinite states of the gaseous mixture, which are a priori possible. In the H curve we can distinguish three parts: the first is formed from the complex of points above the point G, the second from the complex of points between G and F, and the third from the complex of points under F. As one can immediately verify with the aid of relations (6), (7), corresponding to the first part of the H curve (detonation) $D > W > 0$; corresponding to the second part (which represents no physical transformation) D and W assume imaginary values; and last, corresponding to the third part (deflagration) $D > 0$ and $W < 0$.

Further, making use of several considerations about the entropy of the system, one can prove (see for example Schorah[4]) that there exists only one point of the H curve to which corresponds a stable state of the detonation process. This state is analytically determined by the fact that, corresponding to it, the derivative dS/dv of the entropy must be taken equal to zero; graphically

[4] R. L. Schorah, J. Chem. Phys. **3**, 425 (1935).

the stable state is represented by the contact point of the tangent to the curve H from the point (v_1, p_1), characteristic of the state of the unexploded substance. The fact that, corresponding to the stable state, we have

$$D = U + W$$

is of considerable importance, where U denotes the velocity of sound in the mixture of gases resulting from detonation.

2

If we take the equation of state (5) to be known, it is possible to calculate all the quantities ρ, p, T, D, W which characterize, from the physical standpoint, any gaseous explosive, because the pressure of gases deriving from the detonation reaches some thousand atmospheres: the results of theoretical calculations—see for example Lewis[5]—are in very reasonable agreement with experimental facts. On the other hand, in the detonation of solid explosives gaseous mixtures are produced whose pressures can reach above 10^5 atmos. In theoretical calculations one experiences the difficulty that at such extremely high pressures no experimentally proved equation of state is known. In this connection, we shall now show that if we start from the experimental relation between the velocity of detonation D and the density of the unexploded

substance ρ_1, not only can we unequivocally derive the values of the further explosion parameters (W, ρ, p, T) without *a priori* knowledge of the equation of state for the gaseous products, but we can also arrive at such an equation. Writing the unknown equation of state in the very general form

$$pv = r(v)T, \qquad (10)$$

we see indeed that the H curve of the detonation process obeys the equation ($p_1 \ll p$)

$$p = \frac{A}{B(v)v - \frac{1}{2}v_1},$$

where

$$A = \bar{c}_v T_1 + q, \quad B(v) = \frac{\bar{c}_v}{r(v)} + \frac{1}{2}.$$

The stable state, which can be obtained—as we have remarked—by the determination of the contact point of the tangent to the H curve from the initial point (v_1, p_1), is in this case determined by the equation in η:

$$\eta^2 + 2k\eta - (k - \sigma) = 0, \qquad (11)$$

where

$$\eta = \frac{W}{D}, \quad k = \frac{2A}{D^2}, \quad \sigma = \frac{1}{2}\eta(1 - \eta)v_1\frac{(dB/dv)}{B}(k + \eta).$$

σ being very small with respect to k, we can easily solve Eq. (11) following a method of successive approximations.

From the values of η, which we obtain in this way, we derive further the corresponding values

TABLE I. Nitropentaerytrite.

ρ_1 (kg/dm³)	D (m/sec.)	ρ (kg/dm³)	p (kg/cm²)	T (°K)
0.5	3960	0.79	29,600	4670
0.65	4400	1.00	44,900	4840
0.8	4900	1.20	65,000	5050
1.0	5500	1.45	95,300	5320
1.2	6300	1.69	140,500	5720
1.4	7100	1.93	195,500	6170
1.6	7900	2.15	262,800	6670

TABLE II. Tetryl.

ρ_1 (kg/dm³)	D (m/sec.)	ρ (kg/dm³)	p (kg/cm²)	T (°K)
1.00	5480	1.43	91,800	4400
1.28	6510	1.80	160,400	4740
1.45	7220	2.02	218,100	4980
1.54	7375	2.15	242,500	5100
1.61	7470	2.20	259,100	5140

[5] Lewis, Chem. Rev. 10, 49 (1932).

TABLE III. Picric acid.

ρ_1 (kg/dm³)	D (m/sec.)	ρ (kg/dm³)	p (kg/cm²)	T (°K)
1.03	5150	1.47	83,000	3880
1.23	5820	1.72	120,700	4070
1.39	6450	1.93	164,600	4280
1.63	7210	2.25	239,400	4660

TABLE IV. Trinitrotoluene.

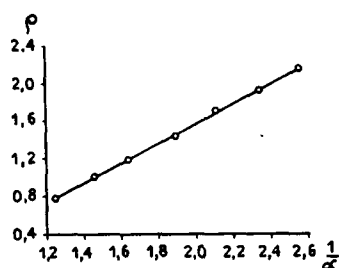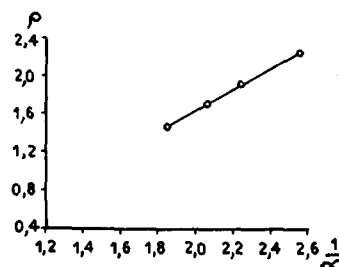| ρ_1 (kg/dm³)	D (m/sec.)	ρ (kg/dm³)	p (kg/cm²)	T (°K)
1.0	4700	1.44	68,700	3210
1.29	5900	1.82	132,800	3610
1.46	6500	2.04	178,000	3860
1.59	6900	2.22	216,200	4020

FIG. 3. Equation of state for detonation gases: nitropentaerytrite.
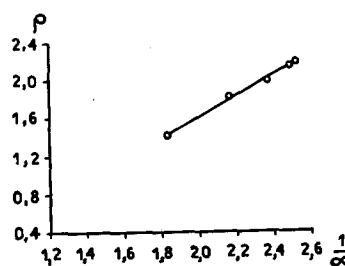

FIG. 5. Equation of state for detonation gases: picric acid.

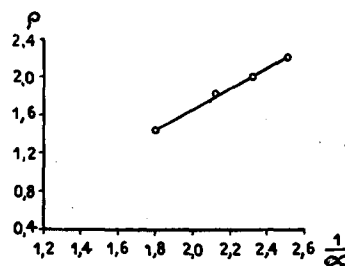FIG. 4. Equation of state for detonation gases: tetryl.

FIG. 6. Equation of state for detonation gases: trinitrotoluene.

of ρ, p, T making use of Eqs. (6)–(8). Following this procedure we have the possibility of establishing the function $r(v)$ and therefore the unknown equation of state.

We have performed numerical computations for several explosives (nitropentaerytrite, tetryl, picric acid, trinitrotoluene) assuming as starting point the experimental relation between the detonation velocity D and the density of explosive, derived from the results of careful measurements performed by Friederich.[6] For the chemical equations of the explosive reactions, characteristic of the detonation processes, we have taken the data from A. Schmidt[7]; the values of the mean specific heats as functions of the temperature, for every gaseous mixture were calculated starting from the data contained in Beyling-Drekopf's book.[8]

Tables I–IV present a summary of the results of our numerical calculations.

From our results we can conclude that the quantities p, v, T of the gaseous mixtures re-

sulting from the several processes of detonation are in good accordance with the equation (due to Van Laar)

$$p[v-\alpha(v)]=nRT, \qquad (12)$$

with

$$\alpha(v) = \frac{b}{1+c/v} = \frac{b}{1+c\rho}, \qquad (13)$$

where the constants b, c have the following numerical values:

nitropentaerytrite: $b=2.08$ $c=2.00$
tetryl: $b=1.81$ $c=1.62$
picric acid: $b=1.96$ $c=1.79$
trinitrotoluene: $b=2.07$ $c=1.88$

In order to illustrate the accuracy with which the equation of state (12) is verified, we have plotted in Figs. 3–6 the values of ρ against the values of $1/\alpha$ for the gaseous mixture of the explosives considered. One can see that the dependence is really linear, as one must expect from Eq. (13).

Finally, attention is called to the fact that the equation of state (12), which we have derived, is suitable only within the range of pressures and temperatures occurring in processes of detonation of solid explosives, that is approximatively from 30,000 to 300,000 atmos., and from 3000 to 7000°K.

[6] W. Friederich, Zeits. ges. Schiess. und Sprengstoffe 28, 2, 51, 80, 143, 213, 244 (1933).

[7] A. Schmidt, Zeits. ges. Schiess. und Sprengstoffe 33, 364 (1938); 34, 8, 37, 80 (1939).

[8] C. Beyling and K. Drekopf, Sprengstoffe und Zündmittel (Julius Springer, Berlin, 1936).