# **Explosives for civil uses — High explosives —**

**Part 15: Calculation of thermodynamic properties**

The European Standard EN 13631-15:2005 has the status of a British Standard

ICS 71.100.30



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#### **Summary of pages**

This document comprises a front cover, an inside front cover, the EN title page, pages 2 to 21 and a back cover.

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## EUROPEAN STANDARD NORME EUROPÉENNE EUROPÄISCHE NORM

## **EN 13631-15**

May 2005

ICS 71.100.30

English version

### Explosives for civil uses - High explosives - Part 15: Calculation of thermodynamic properties

Explosifs à usage civil - Explosifs - Partie 15 : Calcul des propriétés thermodynamiques

Explosivstoffe für zivile Zwecke - Sprengstoffe - Teil 15: Berechnung der thermodynamischen Eigenschaften

This European Standard was approved by CEN on 21 March 2005.

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**Management Centre: rue de Stassart, 36 B-1050 Brussels**

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## **Contents**



## **Foreword**

This document (EN 13631-15:2005) has been prepared by Technical Committee CEN/TC 321 "Explosives for civil uses", the secretariat of which is held by AENOR.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by November 2005, and conflicting national standards shall be withdrawn at the latest by November 2005.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association, and supports essential requirements of EU Directive(s).

For relationship with EU Directive(s), see informative Annex ZA, which is an integral part of this document.

This European Standard is one of a series of standards on *Explosives for civil uses– High explosives.* The other parts of this series are:

*Part 1: Requirements.* 

- *Part 2: Determination of thermal stability of explosives.*
- *Part 3: Determination of sensitiveness to friction of explosives.*
- *Part 4: Determination of sensitiveness to impact of explosives.*
- *Part 5: Determination of resistance to water.*
- *Part 6: Determination of resistance to hydrostatic pressure.*
- *Part 7: Determination of safety and reliability at extreme temperatures.*
- *Part 10: Method for the verification of the means of initiation.*
- *Part 11: Determination of transmission of detonation.*
- *Part 12: Specifications of boosters with different initiating capability.*
- *Part 13: Determination of density.*
- *Part 14: Determination of velocity of detonation.*
- *Part 16: Detection and measurement of toxic gases.*

This document includes a Bibliography.

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#### **Introduction**

Some properties of the explosives used to define their energetic performance on an *a priori* basis are obtained by means of a thermodynamic calculation. The outcome of such calculation, based on the composition and density of the explosive, is dependent on the detonation state considered, the thermodynamic data used and the calculation method itself.

The simplest thermodynamic calculation of explosives is the one for a constant-volume reaction, usually referred to as constant-volume explosion state. Other calculations such as the Chapman-Jouguet (CJ) detonation state are also commonly used, leading to important dynamic values such as detonation pressure and velocity. However, these calculated values are not meaningful in practice for non-ideal industrial explosives. For this reason, only the simple values of energy and amount of gases produced are considered in this European Standard.

#### **1 Scope**

This European Standard specifies a method to calculate the detonation characteristics at the constant-volume explosion state and some parameters derived thereof.

#### **2 Normative references**

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 13857-1:2003; *Explosives for civil uses - Part 1:Terminology* 

#### **3 Terms and definitions**

For the purposes of this European Standard, the terms and definitions given in EN 13857-1:2003 and the following apply.

#### **3.1**

#### **constant-volume explosion state**

detonation point of theoretical nature in which the specific volume of the detonation products is that of the unreacted explosive

#### **3.2**

#### **heat of explosion**

energy released in the chemical reaction of the explosive when the composition of the reaction products is that of the constant-volume explosion state. It is usually given per mass of explosive

#### **3.3**

#### **gas volume**

volume occupied by the detonation product gases, as calculated from the chemical equilibrium composition in the constant-volume explosion state, at a specified condition of temperature and pressure. It is usually given per mass of explosive

#### **3.4**

#### **specific force**

result of the calculation: *n*R*T*, *n* being the number of moles of detonation product gases per mass, R the universal gas constant and *T* the temperature of explosion. It would be equal to the pressure exerted by the detonation gases if the specific volume were unity and the gases behaved as ideal. It is also called in some places specific energy

#### **4 Calculation procedure**

#### **4.1 Thermodynamic Data and Functions**

#### **4.1.1 General**

The thermodynamic properties needed relate to both explosive components and detonation products.

#### **4.1.2 Explosive components**

For each component the following data are required:

*-* Molecular or empirical formula.

#### *-* Energy of formation.

Table 1 shows these values for some explosives components. Whenever the explosive composition include any component not included in such table, the relevant values should be obtained elsewhere, e.g., from a thermochemical data source. In this case, the values used and the source should be reported.



#### **Table 1 - Explosives components**



#### **4.1.3 Detonation products**

Detonation calculations require, in all cases, the following knowledge on detonation products:

- *-* Formula.
- *-* Internal energy or enthalpy of formation at a reference temperature, e.g. 298 K (∆*Ef* 298, ∆*Hf* 298); Table 2 shows these data for some detonation products. Data for other products may be obtained elsewhere. In this case, values used and the source should be reported.

**Table 2 - Detonation products** 

		$\Delta E_f^{298}$	$\Delta H_f^{298}$	
<b>Name</b>	<b>Formula</b>	kJ/mole	kJ/mole	<b>Reference</b>
Ammonia	$H_3N$	$-43,42$	$-45,90$	Chase
Aluminium oxide (I)	$Al_2O_3$ (I)	$-1617$	$-1621$	Chase
Aluminium oxide (s)	$\text{Al}_2\text{O}_3$ (s)	$-1672$	$-1676$	Chase
Calcium chloride (I)	CaCl <sub>2</sub> (I)	$-771,6$	$-774,1$	Chase
Calcium chloride (g)	CaCl <sub>2</sub> (g)	$-471,5$	$-471,5$	Chase
Calcium oxide (s)	CaO (s)	$-633,8$	$-635,1$	Chase
Carbon (s)	C	0	0	
Carbon dioxide	CO <sub>2</sub>	$-393,8$	$-393,8$	Meyer
Carbon monoxide	CO	$-111,9$	$-110,6$	Meyer
Chlorine	Cl <sub>2</sub>	0	0	
Hydrogen	H <sub>2</sub>	0	0	
Hydrogen chloride	<b>CIH</b>	$-92,4$	$-92,4$	Meyer
Iron (III) oxide (s)	$Fe2O3$ (s)	$-821,8$	$-825,5$	Chase
Magnesium oxide (g)	MgO(g)	56,9	58,2	Chase
Magnesium oxide (I)	MgO (I)	$-531,4$	$-532,6$	Chase
Magnesium oxide (s)	MgO(s)	$-600,0$	$-601,2$	Chase
Methane	CH <sub>4</sub>	$-72,4$	$-74,9$	Chase
Nitrogen	$N_2$	0	0	
Nitrogen monoxide	<b>NO</b>	90,3	90,3	Meyer
Oxygen	O <sub>2</sub>	0	0	
Potassium carbonate (I)	$CK2O3$ (I)	$-1127$	$-1131$	Chase
Potassium carbonate (s)	$CK2O3$ (s)	$-1146$	$-1150$	Chase
Potassium chloride (g)	CIK(g)	$-215,9$	$-214,7$	Chase
Potassium chloride (I)	$CIK$ (I)	$-420,6$	$-421,8$	Chase
Potassium chloride (s)	CIK(s)	$-435,4$	$-436,7$	Chase
Silicon dioxide (I)	$O2Si$ (I)	$-900,2$	$-902,7$	Chase

![](_page_10_Picture_284.jpeg)

NOTE 1 (g), (I) and (s) indicate gaseous, liquid and solid state respectively. Where no state is indicated, data are for the gas.

NOTE 2 References are listed in the Bibliography. In many cases, internal energies of formation have been worked out from enthalpy of formation values.

*-* Internal energy or enthalpy as a function of temperature1.

As a minimum, the detonation products listed in Table 2 should be considered, as required, depending on the composition elements. Others may also be included. The detonation products used should be reported.

For the calculation of the equilibrium composition by means of minimization of the free energy of the products, the following is also required to build a chemical potential:

*-* Entropy constant, or entropy at one temperature.

With these basic data, the following ideal thermodynamic functions can be formed; reference state is taken that of the elements in their stable state at 298 K and atmospheric pressure:

*Internal energy* 

For gases.

 $\overline{a}$ 

$$
E_i(T) = \Delta E_{fi}^{298} + (E^T - E^{298})_i = \Delta E_{fi}^{298} + (H^T - H^{298})_i - R(T - 298)
$$

*T* being absolute temperature. For condensed species,

$$
E_i(T) = \Delta H_{fi}^{298} + (H^T - H^{298})_i
$$

*Chemical potential*:

$$
\mu_i^o(T) = \Delta H_{fi}^{298} + (H^T - H^{298})_i - TS_i
$$

 $1$  These can be obtained from Chase (1998), Meyer et al. (2002) and other sources. Polynomial fits are customarily used. The source of the data used should be reported.

#### **EN 13631-15:2005 (E)**

*Entropy*:

$$
S_i(T) = \int_{T}^{C_{pi}} dT + S_{ci}
$$

*Sci* being the integration constant for entropy, a data.

The molar heats (H<sup>T</sup>–H<sup>298</sup>)<sub>i</sub> are usually given as polynomials of T or calculated by integration of the heat capacities *cpi* (also given as polynomials of *T*).

#### **4.2 Equations of state**

#### **4.2.1 Gases**

A suitable equation of state (EOS) for the detonation products is required to calculate the thermodynamic functions.

The following EOS can be used:

- *-* BKW
- *-* H9

a) BKW Equation of state

The BKW EOS has the following form:

$$
\frac{Pv}{RT} = \sigma(X) = 1 + Xe^{\beta X}
$$

where β is a constant, and *X*:

$$
X = \frac{\kappa \sum x_i k_i}{\nu (T + \theta)^{\alpha}}
$$

*v* is the molar gas volume

 $\kappa$ ,  $\alpha$  and  $\theta$  are empirical constants

 $k_i$  is the covolume of *i*-th species and  $x_i$  its mole fraction

Table 3 shows BKW constants and covolumes for several gas species, extracted from Fried and Souers (1996). Additional data may be obtained from Hobbs and Baer (1992).

Other values of the parameters may be used, in which case they shall be reported.

		<b>BKW<sup>a</sup></b>	H <sub>9</sub>
<b>Constants</b>			
$\alpha$		0,5	
β		0,298	
$\theta$ (K)		6620	
$\kappa$ (cm <sup>3</sup> K <sup><math>\alpha</math></sup> /mol)		10,50	
ĸ			$6,35\times10^{-5}$
<b>Covolumes</b>			
Ammonia	$H_3N$	418	0
Calcium chloride	Cl <sub>2</sub> Ca	3 1 8 0	
Carbon dioxide	CO <sub>2</sub>	663	12,5
Carbon monoxide	CO	614	6
Chlorine	Cl <sub>2</sub>	872	
Hydrogen	H <sub>2</sub>	153	0,6
Hydrogen chloride	<b>CIH</b>	570	
Magnesium oxide	MgO	938	
Methane	CH <sub>4</sub>	493	
Nitrogen	$N_2$	376	8,7
Nitrogen monoxide	<b>NO</b>	394	6
Oxygen	O <sub>2</sub>	316	9,9
Potassium chloride	<b>CIK</b>	1810	
Sodium chloride	CINa	2 0 7 0	5
Water	H <sub>2</sub> O	376	6,5

**Table 3 - KW and H9 equations of state parameters and covolumes** 

b) H9 Equation of state

The H9 equation of state has the following form:

$$
\frac{Pv}{RT} = \sigma(X) = 1 + X \frac{d\Phi(X)}{dX}
$$

where

$$
\Phi(X) = X + 0,625\frac{X^2}{2} + 0,287\frac{X^3}{3} - 0,093\frac{X^4}{4} + 0,0014\frac{X^5}{5}
$$

so,

$$
\frac{Pv}{RT} = \sigma(X) = 1 + X + 0.625X^2 + 0.287X^3 - 0.093X^4 + 0.0014X^5
$$

with

$$
X = \frac{\Omega}{\nu T^{0.33}}; \Omega = \kappa \sum x_i l_i; l_i = 2{,}5736 \cdot \frac{N_0}{\kappa} \cdot \sigma_i^3 \left(\frac{\varepsilon_i}{k}\right)^{1/3}
$$

where

- $\kappa$  is constant  $\kappa = 6.35 \times 10^{-5}$
- *xi* is mole fraction of species *i*
- $l_i$  is covolume of species *i* (m $^3\textsf{K}^{1/3}$ mol $^{-1})$
- $N_0$  is Avogadro's number
- $\sigma_i$  (m) is molecular diameter
- $\varepsilon$  *i* s molecular potential well depth (K)

Table 3 shows the values of  $\kappa$  and of the covolumes for some species.

#### **4.2.2 Condensed phases**

Explosives for civil uses are generally near oxygen-balanced, so that small amounts of graphite are formed in detonation states. If the amount of condensed species is not too high, they can be treated as incompressible without much error.

If an equation of state is used for condensed products, it should be reported in the test result.

#### **4.3 Equilibrium calculations**

A minimization of the total free energy of the products should be used for the determination of product composition. The equilibrium composition of a system with specified temperature and volume is so that it minimizes the total Helmholtz free energy.

If incompressible condensed phases are considered, the total free energy is:

$$
F = \sum_{igas} n_i (\mu_i^0 - RT) + RT \sum_{igas} n_i \ln n_i + n_g RT \ln \frac{RT}{P_0 \nu} + F_{imp} + \sum_{icond} n_i \mu_i^0
$$
\n<sup>(1)</sup>

where

*ni* is moles of the *i-th* species per kilogram of mixture

- $\mu_i^0$ is chemical potential of species *i*
- R is Universal gas constant
- *T* is Absolute temperature
- $P_0$  is reference pressure ( $P_0$  = 10<sup>5</sup> Pa =1 bar)
- *V* is specific volume of the gas phase
- *Fimp* is the imperfection term

If BKW EOS is used:

$$
(F_{imp})_{BKW} = n_g R T \frac{e^{\beta X} - 1}{\beta}
$$

If H9 EOS is used:

$$
(F_{imp})_{H9} = n_g \text{RT} \bigg( X + 0.625 \frac{X^2}{2} + 0.287 \frac{X^3}{3} - 0.093 \frac{X^4}{4} + 0.0014 \frac{X^5}{5} \bigg)
$$

If chemical species are assumed to appear either in the gas phase or condensed, but not in both, no phase equilibrium conditions are needed. The minimum of (1), restricted to the conservation of atomic species, gives the equilibrium composition of the mixture, i.e., *ni* .

The equilibrium calculation is a non-linear problem with equality (atom balances) and inequality constraints (non negative mole numbers). Minimization of the free energy function may be done using non-linear optimization with linear restrictions techniques, such as Lagrange multipliers or gradient methods.

The method for obtaining the detonation products composition shall be reported.

#### **4.4 Layout of a calculation scheme**

A description of a suitable calculation method is the following:

a) Calculate explosive formula per kg and the energy of formation, using Table 1. Calculate the internal energy of the explosive  $(E_0)$ . Taking as reference state the elements at 298 K:

$$
E_0 = \sum_{j=1}^{N_s} c_j \Delta E_{jj}^{298} \tag{2}
$$

 $\Delta E\frac{^{298}}{6}$ is the energies of formation per unit mass of the  $N_s$  explosive constituents at 298 K

#### *cj* is their mass fractions

The resulting  $E_0$  is, hence, per unit mass of explosive (e.g. per kilogram).

b) Form the set of product species, depending on the elements present.

c) Assume 
$$
T
$$
 (e.g. 3 000 K).

- c) Compute the thermodynamic data at *T*.
- d) Calculate the product composition, *ni* . This will be determined as that of equilibrium at the calculation temperature and specific volume equal to that of the unreacted explosive, as a constant-volume explosion state calculation is performed.
- e) Solve for *T* the conservation of energy equation.

As no CJ calculation is performed, the energy equation is the only one needed. For the constant-volume explosion state, the energy equation is simply:

$$
E-E_0=0\tag{3}
$$

*E* being internal energy of the products and  $E_o$  internal energy of the explosive, given by Equation (2).

The internal energy of the products *E* is:

$$
E = E_{\text{gas}} + E_{\text{cond}} \tag{4}
$$

where  $E_{gas}$  and  $E_{cond}$  are the total internal energies for the gas and the condensed phases, respectively. For the gas phase:

$$
E_{\rm gas} = \sum_{i \text{gas}} n_i E_i^0 + E_{\rm imp} \tag{5}
$$

where  $E_i^0$ , with the same reference state as above, is calculated as:

$$
E_i^0 = \Delta E_{fi}^{298} + (E^T - E^{298})_i = \Delta E_{fi}^{298} + (H^T - H^{298})_i - R(T - 298)
$$
 (6)

and  $E_{\text{imp}}$  is the imperfection term. If BKW EOS is selected:

$$
(E_{\rm imp})_{\rm BKW} = n_g R T \frac{\alpha T}{T + \theta} (\sigma - 1)
$$

and for H9 EOS:

$$
(E_{\rm imp})_{\rm H9} = n_g \mathbf{R} T \frac{1}{3} (\sigma - 1)
$$

Internal energies of the individual species are molar values.

For the condensed phases, assumed incompressible:

$$
E_{\text{cond}} = \sum_{i \text{cond}} n_i E_i \tag{7}
$$

where

$$
E_i = \Delta H_{fi}^{298} + (H^T - H^{298})_i
$$
 (8)

The energy equation is, finally, from  $(3)$ ,  $(4)$ ,  $(5)$ ,  $(6)$ ,  $(7)$  and  $(8)$ :

$$
\sum_{igas} n_i \Delta E_{fi}^{298} + \sum_{igas} n_i (H^T - H^{298})_i - n_g R(T - 298) + \sum_{icond} n_i \Delta H_{fi}^{298} + \sum_{icond} n_i (H^T - H^{298})_i + E_{imp} - E_0 = 0
$$
\n(9)

Once the composition has been determined, (9) is a function of *T* only.

- f) Redo 4 through 6 until convergence in *T*.
- g) Temperature of explosion at constant volume:  $T_v = T$ .
- h) Obtain the performance parameters:
	- 1) Heat of explosion at constant-volume:

$$
Q_{v} = E_0 - \sum_{i=1}^{N_p} n_i \Delta E_{fi}^0
$$

2) Gas volume at standard temperature and pressure; for this purpose, standard temperature is 273,15 K and standard pressure is 100 kPa:

$$
V_{STP} = 0.0227 n_g
$$

3) Specific force (or specific energy):

$$
f = n_g R T_v
$$

Other parameters may be derived from the calculation results.

#### **5 Report**

The report shall contain the following information:

- a) reference to this European Standard;
- b) energy of formation and gross formula of components not included in this standard, and the source of the data;
- c) detonation products considered;
- d) energy of formation of detonation products not included in this standard, and the source of the data;
- e) source of the detonation products heat functions;
- f) gas equation of state used and parameter set, if required;
- g) condensed equation of stated, if other than incompressible;
- h) method of calculation of detonation products composition;
- i) heat of explosion (kJ/kg), gas volume (m<sup>3</sup>/kg) and specific force (kJ/kg).

## **Annex A**

(informative)

## **Sample calculations**

When variants of the calculation method described in this standard are applied to the compositions listed in Table A.1, the results given in Tables A.2 through A.6 are obtained. The main features of the three calculation methods (A, B, C) are summarised in Table A.7.

![](_page_17_Picture_109.jpeg)

#### **Table A.1 - Sample explosives formulations**

<b>Explosive</b>	A	в	C
Anfo	2586	2654	2 2 9 8
Anfo-Al	3 0 6 0	3 0 8 5	2826
<b>Slurry</b>	2 168	2 2 3 8	1 655
Slurry-Al	2 5 2 2	2610	2 1 6 2
<b>Emulsion</b>	2 0 9 9	2 189	1512
<b>Emulsion-Al</b>	2458	2 5 6 7	1896
Dynamite-1	4 130	4 2 3 7	3696
<b>Dynamite-2</b>	2 2 2 3	2 7 3 4	1 657
Dynamite-3	3 1 5 1	3 2 1 5	2 5 5 6

**Table A.2 - Constant-volume explosion temperature (K)** 

**Table A.3 - Heat of explosion (kJ/kg)**

			<u>.</u>
<b>Explosive</b>	A	B	C
Anfo	3820	3963	3 6 9 0
Anfo-Al	4 6 4 2	4 803	4580
<b>Slurry</b>	3 3 0 7	3466	3 190
Slurry-Al	4 0 1 0	4 1 9 8	3880
<b>Emulsion</b>	3 2 3 6	3 4 3 1	3 0 4 0
<b>Emulsion-Al</b>	3 9 5 2	4 181	3840
<b>Dynamite-1</b>	6 338	6 544	6 2 8 0
Dynamite-2	2766	2 7 3 4	2 5 5 0
Dynamite-3	4 9 8 9	5 1 2 5	4 9 5 0

<b>Explosive</b>	A	B	C
Anfo	998	997	983
Anfo-Al	910	909	895
<b>Slurry</b>	1 0 2 3	1017	1 0 0 8
Slurry-Al	970	952	954
Emulsion	1 0 0 2	983	982
<b>Emulsion-Al</b>	948	917	922
<b>Dynamite-1</b>	752	746	739
<b>Dynamite-2</b>	576	574	599
<b>Dynamite-3</b>	853	851	840

**Table A.4 - STP gas volume (l/kg)** 

#### **Table A.5 - Specific force (kJ/kg)**

![](_page_19_Picture_99.jpeg)

<b>Explosive</b>	A	в	C
Anfo	0,095	0,071	0,137
Anfo-Al	0,036	0,025	0,028
Slurry	0,044	0,022	0,110
Slurry-Al	0,162	0,094	0,504
<b>Emulsion</b>	0,051	0,023	0,123
<b>Emulsion-Al</b>	0,139	0,082	0,491
<b>Dynamite-1</b>	0,109	0,072	0,123
Dynamite-2	0	0	0
Dynamite-3	0,005	0,002	0,002

Table A.6 - CO/CO<sub>2</sub> molar ratio

![](_page_20_Picture_88.jpeg)

![](_page_20_Picture_89.jpeg)

## **Annex ZA**

(informative)

### **Clauses of this European Standard addressing essential requirements or other provisions of EU Directives**

This European Standard has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association and supports essential requirements of EU Directive 93/15/EEC.

WARNING : Other requirements and other EU Directives may be applicable to the product(s) falling within the scope of this standard.

The clauses of this standard are likely to support requirements I.2 and II.1 (a) of Directive 93/15/EEC.

Compliance with this standard provides one means of conforming with the specific essential requirements of the Directive concerned and associated EFTA regulations.

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