A New Way for Computing the Performance Parameters of Propellants with the VLW Equation of State*

Wu Xiong**

The VLW equation of state based on the virial theorem can be used for the calculating not only explosive detonation but also propellant combution. It is shown that the results computed of rocket propellants and gun propellants are reasonably satisfactory.

INTRODUCTION

The VLW equation of state(VLW EOS) based on the virial theorem was presented at the 8th and 9th Symposium(International) on Detonation for computing the detonation performance of explosives in 1985[1] and 1989[2] respectively. It has been shown that the VLW equation of state is of some distinct specialities. First, being truncated arbitrarily, it is valid for a wide range of the pressure from several bars to several hundreds k bars and of the densities from 0.005 g/cm^3 to 3.5 g/cm^3.

Second, the higher virial coefficients may be estimated conveniently from the well known second one. And third, either the intermolecular potential Lennard−Jones or the realistic potential EXP−6 are available. This may lead us to extend the applications of VLW EOS to the products reacted of all the energetic materials. And it may be also expected for studies of the stages of Deflagration to Detonation Transition(DDT) mechanism for propellant or explosive charges including the whole process *i. e.*, Ignition−Burning−Detonation, but in this paper we would like to focus on computing the performance of both rocket propellants and gun propellants.

THE EQUATION OF STATE

The ideal gas equation of state is commonly used to calculate the performance of propellants. For a thorough study, however, the accuracy of the ideal gas equation of state is not satisfying for higher pressure conditions especially for DDT study.

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*Projects supported by the National Natural Science Foundation of China
**Xian Modern Chemistry Research Institute, Xian 710061,China

To use the VLW equation of state which may be vaild for a wide range of pressures and for the products reacted of all energetic materials with a higher degree of accuracy is the aim of this study. The expression of VLW EOS is:

$$\frac{P_v}{RT} = 1 + B^*\left(\frac{b_o}{v}\right) + \frac{B^*}{T^{*1/4}}\sum_{n=3}^{n}(n-2)^{-n}\left(\frac{b_o}{v}\right)^{(n-1)} \qquad (2-1)$$

$$T^* = \sum_i\sum_j x_i x_j T^*_{ij}/\bar{x}^2; \quad T^*_{ij} = (T^*_i T^*_j)^{1/2}$$

$$T^*_i = KT/\epsilon_i; \quad b_o = \sum (x_i/\bar{x})(b_o)_i$$

$$(b_o)_i = (2/3)\pi N\sigma_i^3; \bar{x} = \sum x_i$$

where B^* is the reduced second virial coefficient. T^*, the reduced average temperature; x_i, the number of moles of species i; N, Avogadro's number; k, Boltzmann's constant.

B^* can be expressed in terms of Lennard−Jones potential (L−J) or EXP−6 potential, but we would like to use the L−J potential(6−12) for the combustion problems in this paper, *i. e.*,

$$B^* = \sum_{j=0}^{n}\left[-\frac{2^{j+1/2}}{4j!}\Gamma\left(\frac{j}{2}-\frac{1}{4}\right)T^{*-(2j+1)/4}\right] \qquad (2-2)$$

here ϵ,σ are the parameters of Lennard−Jones potential, given in table 1.

According to the range of pressures, the VLW EOS may be truncated in practical purposes.

For common pressure, we take the VLW EOS *i. e.*,

$$Pv/RT = 1 \qquad (2-3)$$

Table 1 The parameters of Lennard—Jones potential

	Ref.6			This paper		
	σ(Å)	ε/K(K)	b_o (cc/mol)	σ(Å)	ε/K(K)	b_o(cc/mol)
H_2O				2.818	180.0	28.0
H_2	2.87	29.2	29.76	2.868	29.20	29.76
O_2	3.58	117.5	57.75	3.575	117.5	57.75
CO_2	4.07	205.0	85.05	4.070	205.0	85.05
CO	3.763	100.2	67.22	3.763	100.2	67.22
NH_3				3.814	138.0	70.00
NO	3.17	131.0	40.00	3.217	131.0	42.00
N_2	3.698	95.05	63.78	3.698	95.05	63.78
CH_4	3.817	148.2	70.16	3.817	148.2	70.16
HCl	3.305	360.0	45.54	3.305	360.0	45.54
Cl_2	4.400	257.0	107.0	4.400	257.0	107.0
Al(g)				3.165	357.0	40.00

Obviously, in this case, the VLW EOS becomes an ideal gas equation of state.

For moderate pressure (several hundreds bars or so), we may use the first two terms of VLW EOS,

$$\frac{Pv}{RT} = 1 + B^* \frac{b_o}{v} \qquad (2-4)$$

In this case, the VLW EOS becomes van der Waals equation of state.

$$\frac{Pv}{RT} = 1 + B^*\left(\frac{b_o}{v}\right) + \frac{B^*}{T^{*1/4}}\sum_{n=3}^{m}(n-2)^{-n}\left(\frac{b_o}{v}\right)^{(n-1)}, \quad m = 5$$

THERMODYNAMIC FUNCTIONS

The thermodynamic functions $H^\circ - H^\circ_{298}$, S°, and $F^\circ - H^\circ_{298}$ based on a fit from $H^\circ - H^\circ_{298}$ are used in our calculations[1,3]. *i. e., let,*

$$H^\circ - H^\circ_{298} = C_1 + C_2T + C_3T^2 + C_4T^3 + C_5T^4, \qquad (2-6)$$

For slightly high pressure (several kbars or more) like gun propellant combustion, we would like to adopt the first three terms of VLW EOS,

$$\frac{Pv}{RT} = 1 + B^*\frac{b_o}{v} + \frac{B^*}{T^{*1/4}}\left(\frac{b_o}{v}\right)^2 \qquad (2-5)$$

And for very high pressure (several hundreds kbars) like high explosive detonation, we should take the whole VLW EOS *i. e.*,

thus,

$$C^\circ_p = C_2 + 2C_3T + 3C_4T^2 + 4C_5T^3 \qquad (2-7)$$

$$S^\circ = C_6 + C_2\ln T + 2C_3T + 3/2\,C_4T^2 + 4/3\,C_5T^3 \qquad (2-8)$$

$$-(F^\circ - H^\circ_{298}) = -C_1 + C_6T + C_2T(\ln T - 1) + C_3T^2 + 1/2C_4T^3 + 1/3C_5T^4 \qquad (2-9)$$

To suit the uses over a wide range of temperatures, a set of coefficients was obtained for each of two temperature intervals, 300° to 1000° K and 1000° K to 5500° K. Each was forced to give the same values for the functions at the common point, 1000° K.

CALCULATIONS

To calculate the rocket performance parameters, following assumptions are used: one-dimensional form of the continuity, energy, and monentum equations; complete combustion; adiabatic combustion; homogeneous mixing; isentropic expansion, and the

equilibrium to be attained for the combustion products.

As the combustion process is isoenthalpic, we have,

$$\sum (x_c)_i[(H^\circ - H^\circ_{293})_i + (\Delta H^\circ_{fc})_i] + H' = \sum n_j(\Delta H^\circ_f)_j \qquad (3-1)$$

where

n is the molar components of propellant; (ΔH°_f) is the heat of formation of propellant.

x_c is the molar species in combustion chamber;

ΔH°_{fc} is the heat of formation of species in combustion chamber.

ΔH°_f is the heat of formation of propellant components.

The right hand side of *Eq*.(3−1) is total enthalpies of propellant components .The left hand side of *Eq*. (3−1) is total enthalpies of species in combustion chamber composed of two terms , *i. e.*, $\Sigma (x_c)_i [(H^\circ - H^\circ_{293})_i + (\Delta H^\circ_{fc})_i]$ and H'. The former belongs to the part of ideal gases, the latter belongs to the part of nonideal gases , which is expressed by the VLW EOS[1,2].

As the expansion process is isentropic, we have,

$$\sum (x_c)_i(s^\circ_c)_i + s'_c = \sum (x_e)_j(s^\circ_e)_j + s'_e \qquad (3-2)$$

The left hand side of *Eq*.(3−2) is total entropies of species in combustion chamber; the right hand side is those in nozzle exit. Each consists of two terms, the former belongs to the part of ideal gases,the latter, the part of nonideal gases described by VLW EOS[1,2].

The basic parameters in combustion chamber like temperature T_c, species x_c, enthalpy H_c and entropy Sc can be calculated from *Eq*.(3−2).

Then by using the well known formulae of rocket propellant performance, all the parameters can be obtained conveniently as listed in table 2 and 3.

Concerning the calculations of gun performance, the assumption is based on an isointernal energetic combustion process, *i. e.*,

$$\sum x_i E_i + E^* = \sum m_j E_j \qquad (3-3)$$

The right hand side of *Eq*.(3−3) is total internal energy of gun propellant components. The left hand side of *Eq*.(3−3) is total internal energy of combustion species composed of two terms: $\Sigma x_i E_i$ represents the ideal gas part, and E^* represents the nonideal gas part, which may be expressed by VLW EOS[1,2].

Using the formulae of gun propellant performance, similarly , all the parameters can be calculated as listed in table 4.

COMPUTED RESULTS

By using the general FORTRAN VLW code, the performance parameters of rocket propellants and gun propellants are computed as listed in table 2−4.

From table 2, it can be seen that the theoretical specific impulse I_s computed is more than that of experimental results. This fact is foreseen due to the assumptions being made such as adiabatic combustion and equilibrium to be attained instantaneously during expansion. In spite of this, the theoretical specific impulse has been playing an important role in the research of rocket propellants.

In table 4, the pressuers p_v of gun propellant gases are as high as several kbars. In this case, the higher pressure gases deviate much from the ideal equation of state. And we may imagine that the deviation increases with increasing loading density. Let's take the first composition of table 4 for an investigation.

From *Eq*.(2−5):

$$\frac{Pv}{RT} = 1 + B^* \frac{b_o}{v} + \frac{B^*}{T^{*1/4}}\left(\frac{b_o}{v}\right)^2$$

If density ρ_o =0.2 (as listed in table 4),then

Pv/RT=1+0.246+0.048

=1.294 (P_v=2.618 *kbars*).

If density ρ_o =0.3, then

Pv/RT=1+0.368+0.109

=1.477 (Pv=4.465 kbars)

If density ρ_o =0.4, then

Pv/RT=1+0.49+0.193

=1.683 (Pv=6.755 kbars)

It will be seen from this fact that a nonideal equation of state should be required for the calculations. This is why we would like to adopt our VLW EOS, the general nonideal equation of state for the propellant combustion studies at higher pressures.

CONCLUSION

1. VLW EOS is an approach of the perfect theoretic virial equation of state. Its principal feature

Table 2 Comparison of the computed results of the rocket propellant performance of this paper with the experimental data and those of reference

	HMX/NH_4ClO_4/Al/others			HMX	
	This paper	ISBKW*	EXPL'T**	This paper	ISBKW*
Input Data:					
C:	11.80182	11.80182		13.506	13.506
H:	22.33559	22.33559		27.011	27.011
N:	11.89068	11.89068		27.011	27.011
O:	27.96811	27.96811		27.011	27.011
Cl:	0.893640	0.893640			
Al:	7.040427	7.040427			
ΔH°_f:	−303.4	−227.56*		60.539	147.28*
pc:	68.94730	68.94730	68.94730	68.947	68.947
pe:	1.013250	1.013250	1.013250	1.0132	1.0132
Output results:					
T_c:	4368.9	4040.7		3414.6	3224.6
T_e:	2566.9	2563.4		1540.4	1632.2
I_s:	272.0	271.0	256.0	266.1	266.5
C^*:	1633.6			1640.8	
u:	2672.3			2609.8	
C_f:	1.6318			1.5905	
Q_p:	1677.7			1247.9	
γ:	1.189			1.232	
H_c:	−303.1			60.54	
H_e:	−115.6			−753.4	
S_c:	217.8			249.1	

I_s is the theoretical specific impulse in units of sec. C^* is the characteristic velocity in m/s. u is exhausst speed in m/s. C_f is thrust coefficiency. Q_p is heat of explosion at constant pressure in J/g. T_c is combustion temperature in $K_\circ$ T_e is exhaust temperature in $K_\circ$ γ is the ratio of constant pressure specific heat C_p to constant volume specific heat C_v. pc is the combustion chamber pressure in bars. pe is the exhaust pressure in bars. H_c is the enthalpy of combustion chamber in kcal/kg. H_e is the enthalpy of exhaust in kcal/kg. S_c is the entropy of combustion chamber in cal/kg °k, which equals to the entropy of exhaust.

*Computed by using the ISBKW code[4]. ΔH°_f is the heat of formation of FORTRAN BKW code, in units of kcal/kg must to be used in the values of element (O°K) to the species (O°K)[4,7], here −303.14 and 60.539 at 298°K equal to −227.56 and 147.28 at O°K respectively.

**This work

is that the higher virial coefficients can be estimated from the well known second one, which can be expressed in terms of the Lennard−Jones potential.

2. The VLW EOS can be used for the predicting not only the detonation properties of explosives[1,2] but also the combustion performance of both rocket propellants and gun propellants. The computed results are reasonably satisfactory.

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Table 3 Comparison of the computed species (mole/kg) in combustion chamber and in exhaust for HMX of this paper with those of ISBKW

	Combustion chamber		Exhaust	
	This paper	ISBKW*	This paper	ISBKW*
H_2O	9.7601	8.8291	8.4153	8.4835
H_2	3.7236	3.8437	5.0902	5.0211
O_2	0.0995	0.0357	0.0000	0.0000
CO_2	3.3704	3.3122	5.0897	5.0210
CO	10.136	10.194	8.4163	8.4850
NH_3	0.0002	0.0002	0.0000	0.0000
NO	0.1539	0.1087	0.0000	0.0000
N_2	13.428	13.451	13.505	13.505
H	0.0015	0.4810	0.0000	0.0012
OH	0.0201	1.1837	0.0000	0.0005

*Computed by using the ISBKW code[4].

Table 4 Comparison of the computed results of the gun propellant performance of this paper with those of experimental data or with those of reference.

	NC/NQ/NG/OTHERS		NC/RDX/OTHERS		NC/NG/TAGN/RDX 15/15/60/10	
	This paper	EXP'1*	This paper	EXP'1*	This paper	Ref.5
Input data:						
C:	15.901				10.149	
H:	32.214				42.355	
N:	23.879				31.340	
O:	27.175				24.755	
ΔH°_f:	−35.8		−35.83		−18.428	
ρ_o :	0.2	0.2	0.2	0.2	0.2	
Output results:						
T_v:	2771		3506.2		3138.6	3031
F_v:	1012.8	1012	1227.1	1226	1125	1202
p_v:	2.618		3.147		3.157	
Q_v:	857.0	888.0	1126.5	1120.0	1108.3	
$\bar{x}$:	43.92		42.10	42.34	47.0	
γ	1.247		1.233		1.237	
f_x:	1.294		1.280		1.288	
B_2:	0.246		0.238		0.242	
B_3:	0.048		0.042		0.046	

F_v is the impetus in units of J/kg. T_v, flame temperatute in K. P_v, the pressure in kbar. Q_v, explosion heat at constant volume in kcal/kg. $\bar{x}$, moles of combustion species in mole/kg. γ, the ratio of constant pressure specific heat C_p to constant volume specific heat C_v. fx represents the left side of *Eq.*(2—5). B_2 represents the term $B^*(b_o/V)$ of *Eq.*(2—5). $B3$, $B^*/T^{*1/4}(b_o/V)^2$ of Eq.(2—5).
ΔH°_f is the heat of formation in kcal/kg. ρ_o , density, in g/cc.
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