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Citation: [The Journal of Chemical Physics](#) **16**, 1081 (1948); doi: 10.1063/1.1746729

View online: <http://dx.doi.org/10.1063/1.1746729>

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centages of dissociation for a total pressure of one atmosphere are given in Table VIII.

The writer wishes to express his thanks for the computing assistance rendered by the following members of Dr. Bengt Carlson's computing group: Josephine Elliott, Max Goldstein, Margaret Johnson, Nell Lane, Marian Peterson, and Alice Snowden.

This paper is based on work performed at the Los Alamos Laboratory of the University of California under Government Contract W-7405-eng-36 and the information contained therein will appear in Division V of the National Nuclear Energy Series (Manhattan Project Technical Section) as part of the contribution of the Los Alamos Laboratory.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 16, NUMBER 11 NOVEMBER, 1948

Fugacity Determinations of the Products of Detonation

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(Received June 2, 1948)

By employing the equation of state derived from the hydrodynamic theory and observed detonation velocities, the thermodynamic equilibrium constant $K_p(T)$ is derived in terms of the concentrations of the various gases comprising the products of detonation and the co-volume $\alpha(v)$, which may be evaluated for any known or assumed density of the products of detonation. A reiteration method is developed for solving simultaneously as many equilibria as is necessary to define completely the composition of the products of detonation. The application of the theory is illustrated by calculations for TNT which are compared with experimental data as well as results obtained from the approximate partial pressure method. Calculations are presented for several additional explosives.

THE application of the hydrodynamic theory of detonation in studies of explosives requires, in general, a knowledge of the products of detonation from which to calculate the essential thermodynamic properties, e.g., the number of moles (n) of gas produced per kilogram of explosive, the heat of explosion at constant volume (Q), the constant volume heat capacity (C_v), etc. The calculation of products of detonation in most explosives is not a simple matter, however, because the mixture may frequently consist of quite a large number of different gases interacting with each other, presumably according to the laws of thermodynamic equilibrium. It is thus necessary in an accurate treatment to solve simultaneously a series of equations involving the equilibrium constants of all of the reactions involved in determining the equilibrium mixture. The problem is further complicated by the fact that in a thermodynamically exact solution one must make use of the activity of the

various components rather than the concentration or partial pressure in the thermodynamic equilibrium constants. In the particular case of gaseous explosives the activity or partial fugacity is practically equal to the partial pressure because the temperature and pressure conditions in these cases are such that the ideal equation of state,

$$pv = nRT, \quad (1)$$

applies with the required accuracy for practical applications. Lewis and Friauf² carried out calculations of products of detonations for some gaseous explosives taking into account the necessary equilibria, and obtained quite accurate correlations between calculated detonation velocities obtained by application of these data and experimental velocities. This work helped to demonstrate not only the validity of the hydrodynamic theory and of the ideal gas law as applied to gaseous explosives, but also that

¹ Now at the University of Utah, Salt Lake City, Utah.

² B. Lewis and J. B. Friauf, *J. Am. Chem. Soc.* **52**, 3905 (1930).

chemical equilibrium exists between the products of detonation in the detonation wave of gaseous explosives.³

Regarding condensed explosives, it is not valid to employ partial pressures in carrying out calculations of the equilibrium composition of the product gases because detonation pressures are thousands of times higher than in gaseous explosives. As a matter of fact, in some cases the total fugacity may be of the order of 10^4 times higher than the total pressure under the conditions occurring in the detonation wave of some high density explosives. Despite this fact, results obtained by the use of partial pressures rather than activities have been surprisingly successful in many applications of theoretical calculations.⁴⁻⁶ In many cases, however, serious errors have resulted from the use of the approximation methods.

Brown⁶ has developed a systematic method for taking into account as many as eleven equilibrium equations although his method employs the partial pressure approximation. Since Brown's work, the hydrodynamic theory has been worked out in considerable detail, making possible the

evaluation of the equation of state applying to the product gases in detonation.⁷⁻¹²

Considerations discussed in reference (7), particularly a comparison of experimental and calculated detonation temperatures, support the assumption that an equation of state of the form

$$pv = nRT + \alpha(v)p \quad (2)$$

applies in detonation. Here $\alpha(v)$ is a co-volume factor depending only on the specific volume, v . The present article describes the development of a method of calculation of the products of detonation, similar to Brown's method, but employing through the equation of state (2) partial fugacities instead of partial pressures in the thermodynamic equilibrium constants. The method is based on the process of reiteration in which any desired number of chemical equilibria may be taken into consideration. Fugacity calculations of the products of detonation have also been carried out by Brinkley and Wilson⁹ and others, based, however, on different equations of state than (2).

THERMODYNAMIC RELATIONS

The various chemical equilibria may be expressed by the equation



where the n_iA_i refer to reactants, and the m_kB_k to products. The thermodynamic equilibrium constant may then be written in the form

$$K_p(T) = \frac{f_{A_1}^{n_1} f_{A_2}^{n_2} \cdots}{f_{B_1}^{m_1} f_{B_2}^{m_2} \cdots} = \prod_i f_i^{\nu_i}, \quad (4)$$

where the Lewis¹³ fugacity f is used for the activity, f_i being the partial fugacity of the i th component of the gaseous mixture, and ν_i the coefficient of this component in (3). The total fugacity is related to the pressure and specific

TABLE I. Values of γ and $e^{\Delta \nu \gamma}$ for various densities of products of detonation.*

Density	a	γ	e^γ	$e^{2\gamma}$	$e^{\gamma/2}$
0		0	1	1	1
0.5	1.089	0.95	2.59	6.69	1.62
0.60	0.829	1.22	3.39	11.47	1.84
0.70	0.633	1.52	4.57	20.9	2.14
0.80	0.5	1.85	6.36	40.5	2.53
0.90	0.396	2.22	9.21	84.8	3.03
1.00	0.32	2.67	14.44	209	3.82
1.10	0.261	3.13	22.9	524	4.81
1.20	0.216	3.65	38.5	1.48×10^3	6.23
1.30	0.179	4.20	66.7	4.45×10^3	8.17
1.40	0.153	4.79	120.3	1.45×10^4	11.02
1.50	0.130	5.39	219	4.80×10^4	14.88
1.60	0.112	6.05	425	1.81×10^5	20.7
1.70	0.095	6.78	881	7.76×10^5	29.7
1.80	0.085	7.44	1.71×10^3	2.91×10^6	41.3
1.90	0.077	8.01	3.01×10^3	9.06×10^6	55.2
2.00	0.070	8.60	5.43×10^3	2.95×10^7	73.7
2.10	0.064	9.15	9.43×10^3	8.88×10^7	97.5
2.20	0.059	9.69	1.62×10^4	2.61×10^8	127.7

* These data were calculated by Mr. R. E. Lunn, Eastern Laboratory.

³ B. Lewis and G. von Elbe, *Combustion, Flames, and Explosions of Gases* (The Macmillan Company, New York, 1938).

⁴ A. Schmidt, *Zeits. ges. Schiess-Springstoffw.* **29**, 259 (1934).

⁵ J. Roth, *Zeits. ges. Schiess-Springstoffw.* **35**, 193 (1940).

⁶ F. Brown, Bureau of Mines Tech. Pub. No. 632.

⁷ M. A. Cook, *J. Chem. Phys.* **15**, 518 (1947).

⁸ G. B. Kistiakowsky and E. B. Wilson, Jr., O.S.R.D. Report No. 69.

⁹ S. R. Brinkley and E. B. Wilson, Jr., O.S.R.D. Reports Nos. 905, 1231, 1510, 1707.

¹⁰ S. Paterson, *Research* **1**, 221 (1948).

¹¹ G. Morris and H. Thomas, *Research* **1**, 132 (1947).

¹² P. Caldirola, *J. Chem. Phys.* **14**, 738 (1946).

¹³ G. N. Lewis and M. Randall, *Thermodynamics and Free Energy of Chemical Substances* (McGraw-Hill Book Company, Inc., New York, 1923).

TABLE II. Equilibrium constants.

K_i	K_1	K_2	K_3	K_4	K_5	K_6	K_7	K_8
Reaction ↓ Temp. - °K	$\text{H}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{H}_2\text{O}$	$\frac{1}{2}\text{H}_2 + \text{CH} \rightleftharpoons \text{H}_2\text{O}$	$\text{H} \rightleftharpoons \frac{1}{2}\text{H}_2$	$\text{O} \rightleftharpoons \frac{1}{2}\text{O}_2$	$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$	$\text{N} \rightleftharpoons \frac{1}{2}\text{N}_2$	$2\text{NO} \rightleftharpoons \text{N}_2 + \text{O}_2$	$2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$
2000	7.2×10^{-6}	9.5×10^{-6}	4.4×10^{-5}	1.7×10^{-5}	4.55		4.0×10^{-4}	26
2400	8.3×10^{-5}	1.4×10^{-4}	3.9×10^{-4}	2.1×10^{-4}	5.8		0.0025	112
2800	4.7×10^{-4}	9.0×10^{-4}	1.83×10^{-3}	1.2×10^{-3}	6.6		0.0092	370
3200	1.66×10^{-3}	3.64×10^{-3}	5.80×10^{-3}	4.42×10^{-3}	7.3	7.0×10^{-5}	0.0244	815
3600	4.52×10^{-3}	1.09×10^{-2}	0.0143	0.0129	8.1	3.0×10^{-4}	0.0502	1410
4000	9.9×10^{-3}	2.54×10^{-2}	0.0292	0.0270	8.2	1.0×10^{-3}	0.100	2360
4400	0.028	0.049	0.053	0.052	8.3		0.166	3750
4800	0.082	0.075	0.083	0.087	8.55		0.247	5550
5200	0.143		0.120	0.131	8.85			
5600	0.512		0.165		9.15			

K_i	K_9	K_{10}	K_{11}	K_{12}	K_{13}	K_{14}	K_{15}	K_{16}
Reaction ↓ Temp. - °K	$\text{O} + 2\text{CO} \rightleftharpoons 2\text{CO}_2$	$\text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2$	$\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$	$\frac{K_{11}}{K_5}$	$K_2 K_5$	$(K_9 K_7)^{\frac{1}{2}}$	$\frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2 \rightleftharpoons \text{NH}_3$	$\text{HCN} \rightleftharpoons \text{C} + \frac{1}{2}\text{N}_2 + \frac{1}{2}\text{H}_2$
2000		0.680	0.120	0.0254	4.5×10^{-5}		32	0.0515
2400		0.324	0.018	0.003	8.3×10^{-4}	2.5×10^{-5}		0.170
2800	1.05×10^{-5}	0.192	0.005	7.3×10^{-4}	6.3×10^{-3}	3.1×10^{-4}		0.440
3200	1.66×10^{-4}				0.0350	2.0×10^{-3}		0.900
3600	0.00141				0.0905	8.6×10^{-3}		1.560
4000	0.0077				0.225	0.028	97	2.350
4400	0.104				0.406	0.132		
4800	0.470				0.641	0.327		
5200	1.60							
5600	22.00							

volume by the equation

$$nRT \left(\frac{d \ln f}{dp} \right)_T = v \quad (5)$$

which from Eq. (2) becomes

$$nRT \left(\frac{d \ln f}{dp} \right)_T = \frac{nRT}{p} + \alpha. \quad (6)$$

Integration of (6) between pressure limits of zero and p gives

$$\frac{f}{p} = \exp \frac{1}{nRT} \int_0^p \alpha dp. \quad (7)$$

The partial fugacity of the i th component is related to the total fugacity by the equation

$$f_i = f N_i, \quad (8)$$

where N_i is the mole fraction of the i th component in the mixture. Multiplying and dividing the left side of (7) by N_i and taking the ν_i th power of both sides gives

$$\left(\frac{f_i}{p N_i} \right)^{\nu_i} = \exp \frac{\nu_i}{nRT} \int_0^p \alpha dp. \quad (9)$$

Equation (4) may now be written

$$\prod_i f_i^{\nu_i} = \prod_i p N_i \exp \frac{\Delta \nu}{nRT} \int_0^p \alpha dp = K_p(T), \quad (10)$$

where

$$\Delta \nu = n_1 + n_2 + \dots - m_1 - m_2 - \dots. \quad (11)$$

In order to make use of Brown's developments a new form of the equilibrium constant may be defined as follows:

$$K_i = K_p \left(\frac{1.2181}{T} \right)^{\Delta \nu}. \quad (12)$$

Now

$$p N_i = \frac{N_i nRT}{a} = \frac{A_i}{a} \frac{T}{1.2181}, \quad (13)$$

where $a = v - \alpha$, and A_i may be any of the A_i 's or B_k 's in Eq. (3) expressed in moles per 100. g of explosive while " a " has the dimensions of liters per kilogram as defined by Brown (p expressed here in atmospheres). Substituting Eqs. (12) and (13) in (10) gives

$$K_i a^{\Delta \nu} = \prod_i A_i^{\nu_i} \exp \Delta \nu y, \quad (14)$$

TABLE III. Definitions of equilibrium constants of Table II.

$$\begin{aligned}
K_1 &= ((\text{H}_2)(\text{O}_2)^{1/2}/(\text{H}_2\text{O})) \cdot e^{v/2}/a^{1/2} \\
K_2 &= ((\text{H}_2)^{1/2}(\text{OH})/(\text{H}_2\text{O})) \cdot e^{v/2}/a^{1/2} \\
K_3 &= ((\text{H})/(\text{H}_2)^{1/2}) \cdot e^{v/2}/a^{1/2} \\
K_4 &= ((\text{O})/(\text{O}_2)^{1/2}) \cdot e^{v/2}/a^{1/2} \\
K_5 &= (\text{CO})(\text{H}_2\text{O})/(\text{CO}_2)(\text{H}_2) \\
K_6 &= ((\text{N})/(\text{N}_2)^{1/2}) \cdot e^{v/2}/a^{1/2} \\
K_7 &= (\text{NO})^2/(\text{O}_2)(\text{N}_2) \\
K_8 &= (\text{CO}) \cdot e^{v/2}/a \\
K_9 &= (\text{O}_2) \cdot e^{v/2}/a \\
K_{10} &= ((\text{CH}_4)/(\text{H}_2)^2) \cdot a/e^v \\
K_{11} &= ((\text{CH}_4)(\text{H}_2\text{O})/(\text{CO})(\text{H}_2)^2) \cdot a^2/e^{2v} \\
K_{12} &= K_{11}/K_5 \\
K_{13} &= K_2 K_5 \\
K_{14} &= (K_3 K_7)^{1/2} \\
K_{15} &= ((\text{H}_2)^{1/2}(\text{N}_2)^{1/2}/(\text{NH}_3)) \cdot e^{v/2}/a \\
K_{16} &= (\text{HCN})/(\text{H}_2)^{1/2}(\text{N}_2)^{1/2}
\end{aligned}$$

where

$$y = \frac{1}{nRT} \int_0^p \alpha dp = \int_{-\infty}^v d\left(\frac{1}{v-\alpha}\right). \quad (15)$$

Equation (14) differs from the approximate partial pressure equation by the factor $\exp \Delta v y$ which actually is unity for the most important equilibrium involved in a large number of explosives, namely, the water gas equilibrium. In many explosives, in fact, the partial pressure and fugacity methods give practically identical results for this reason.

In view of the observation discussed in reference (7), that α is the same function of v for all explosives, a conclusion which has been verified in a large number of cases involving widely different type of explosives, y (Eq. (15)) will also be the same function of v for all explosives and may be evaluated from the α vs. v data of Fig. 1 of reference 7. The values of y corresponding to various values of v have been evaluated by R. E. Lunn from a plot of α against $1/(v-\alpha)$ whose results are given in Table I.

Table II gives $K_i(T)$ data taken largely from Brown⁶ and Schmidt,⁴ although some of the data were extrapolated from curves drawn from lower temperature data and should not be regarded as entirely accurate.

METHOD OF CALCULATION

The following method of calculating the products of detonation is modeled somewhat after the method of Brown⁶ which is especially convenient for use with the equation of state (2). The equilibrium constants of Table II are in a

form such that one need only introduce the factor (a) as shown by Eq. (4) to convert from partial pressures to concentrations. We will consider in the present study only explosives containing carbon, oxygen, hydrogen, and nitrogen. Other types of explosives may be worked into the theory readily but, in general, it is unnecessary to do so, since when other atomic constituents are present one may generally decide what products of detonation are formed from them without taking their thermodynamic equilibria into consideration.

The atom balances of the explosive composition may be expressed as follows:

$$\text{C}_0 = \text{CO}_2 + \text{CO} + \text{CH}_4 + \text{HCN} + 2\text{C}_2\text{N}_2 + \dots, \quad (16a)$$

$$\text{H}_0 = 2\text{H}_2\text{O} + 2\text{H}_2 + \text{H} + \text{OH} + 4\text{CH}_4 + \text{HCN} + 3\text{NH}_3 + \dots, \quad (16b)$$

$$\text{N}_0 = 2\text{N}_2 + \text{N} + \text{NO} + \text{HCN} + 2\text{C}_2\text{N}_2 + \text{NH}_3 + \dots, \quad (16c)$$

$$\text{O}_0 = 2\text{O}_2 + \text{O} + \text{NO} + \text{CO} + 2\text{CO}_2 + \text{H}_2\text{O} + \text{OH} + \dots. \quad (16d)$$

Four key equations may be derived from (16) by solving for CO, H₂, N₂, and a new oxygen balance expression, giving

$$\text{CO} = B_1 \left[1 - \frac{\text{CH}_4 + \text{C} + \text{HCN} + 2\text{C}_2\text{N}_2 + \dots}{\text{C}_0} \right], \quad (17a)$$

$$\text{H}_2 = B_2 \left[1 - \frac{\text{H} + \text{OH} + 4\text{CH}_4 + \text{HCN} + 3\text{NH}_3}{\text{H}_0} \right], \quad (17b)$$

$$\text{N}_2 = \frac{\text{N}_0}{2} \left[1 - \frac{\text{N} + \text{NO} + \text{HCN} + \text{NH}_3 + 2\text{C}_2\text{N}_2}{\text{N}_0} + \dots \right], \quad (17c)$$

$$\begin{aligned}
\Delta = & -\text{CO} - \text{H}_2 - \frac{\text{H}}{2} - 2\text{C} - 5/2\text{HCN} - 4\text{C}_2\text{N}_2 \\
& + 4\text{CH}_4 + \frac{\text{OH}}{2} + 2\text{O}_2 + \text{O} + \text{NO} + \dots. \quad (17d)
\end{aligned}$$

Here Δ is the oxygen balance,

$$B_1 = \frac{C_0 x}{1+x}, \quad B_2 = \frac{\frac{H_0}{2} x}{K_5 + x},$$

and $x = \text{CO}/\text{CO}_2$. The derivatives of these functions are given by Brown. The dimensions of (a) used by Brown was liters/kg, while the atom balances were expressed in g atoms/100 g of explosive. This convention is retained here. In terms of the K_i of Table III, Eqs. (17a), (b), (c) may be written

$$\text{CO} = B_1 \left(1 - \frac{K_{12}(\text{CO})(\text{H}_2)^2 e^{2\nu}}{a^2 C_0} - \frac{N_2^{\frac{1}{2}} \text{H}_2^{\frac{1}{2}} K_{16}}{C_0} - \dots \right), \quad (18a)$$

$$\text{H}_2 = B_2 \left\{ 1 - \frac{a^{\frac{1}{2}} \text{H}_2^{\frac{1}{2}} \left(K_3 + \frac{K_{13}}{x} \right)}{e^{\nu/2} \text{H}_0} - \frac{4K_{12}x(\text{CO})(\text{H}_2)^2 e^{2\nu}}{\text{H}_0 a^2} - \frac{N_2^{\frac{1}{2}} \text{H}_2^{\frac{1}{2}} K_{17}}{\text{H}_0} - \dots \right\}, \quad (18b)$$

$$\text{N}_2 = \frac{N_0}{2} \left[1 - \frac{N_2^{\frac{1}{2}} a^{\frac{1}{2}} K_6}{N_0 e^{\nu/2}} - \frac{a^{\frac{1}{2}} N_2^{\frac{1}{2}} K_{15}}{x N_0 e^{\nu/2}} - \frac{N_2^{\frac{1}{2}} \text{H}_2^{\frac{1}{2}} K_{17}}{N_0} \right]. \quad (18c)$$

The values of (a) and $e^{\Delta \nu}$ may be determined from the conditions under which the computations are to be made, i.e., the known or assumed density. One may then proceed as follows:

Step I. A trial temperature is taken. It is convenient first to estimate this temperature from some approximate calculation, e.g., by writing approximate chemical equations for the explosive reaction, or one may make a rough calculation assuming only the water gas equilibrium (K_5) to be important.

Step II. Find the value of x (by a process of successive approximations) by means of Eqs. (18a), (b), (c) together with whatever auxiliary equilibrium equations (see Table III) are needed to make a complete set, such that Eq.

(17d) gives the same value of Δ as the equation

$$\Delta = \text{O}_0 - 2C_0 - \frac{H_0}{2}. \quad (19)$$

Step III. When the value of x is found such that Eqs. (17d) and (19) give identical results for the oxygen balance, one may compute from the composition obtained the heat of explosion Q and the average heat capacity \bar{C}_v between T_0 and T which will then allow one to derive T for adiabatic explosion, by the equation

$$T = Q/\bar{C}_v + T_0 \quad (20)$$

or, when dealing with the detonation wave conditions, by the Eq. (16), reference 7, namely,

$$T_2 = (Q + T_1 \bar{C}_v) \beta / (\beta \bar{C}_v - \frac{1}{2} n R). \quad (21)$$

Step IV. Repeat steps II and III until the temperature calculated from (20) or (21) agrees with that used in the computations in step II.

In case of large oxygen deficiency, the method of calculation may conveniently be altered to take into account the relative importance of the coke oven equilibrium, (K_8). The selection of a particular x then immediately fixes the values of both CO and CO_2 . The remaining C_0 may be then distributed: (a) as CH_4 which may be computed from Eq. (7), Table III; (b) the carbon remaining may be considered to go into HCN until Eq. (16), Table III, is satisfied; (c) any C_0

TABLE IV. Products of detonation of TNT from theoretical fugacity and partial pressure methods, and Haid and Schmidt's experimental method.

I. = 1.59 g/cc products	A. "Explosion" state		Exp. Haid and Schmidt	B. "Detonation" wave state	
	fugacity method	partial pressure		fugacity method	partial pressure method
CO (moles/kg)	9.4	15.9	9.39	1.7	15.5
CO ₂	6.8	3.2	5.47	9.7	3.4
H ₂	0.6	2.9	1.63	0.07	2.7
H ₂ O	3.4	4.3	6.09	3.1	4.2
N ₂	5.0	5.2	—	4.4	4.0
CH ₄	2.2	1.25	0.42	1.1	0.7
NH ₃	1.1	0.13	1.5	3.4	0.1
HCN	2.0	2.65	0.32	1.0	5.3
Carbon	10.4	7.8	14.6	16.3	5.9
n (moles gas/kg)	30.5	35.6	—	24.5	35.8
Q	1120	860	—	1105	770
C_v	0.342	0.317	—	0.338	0.326
T_2	3420	2975	—	4150 (T_2)	3300 (T_2)
II. = 1.0 g/cc					
CO	16.8	18.2	17.0	16.3	23.1
CO ₂	3.5	2.0	2.84	2.8	0.9
H ₂	2.5	4.3	2.49	1.5	4.4
H ₂ O	2.6	3.2	3.77	4.5	1.3
N ₂	5.5	5.7	4.75	4.6	5.1
CH ₄	1.9	1.2	0.1	2.3	1.8
NH ₃	0.8	0.1	2.85	0.7	0.2
HCN	1.4	1.72	0.47	3.2	2.9
Carbon	7.1	7.3	10.0	5.9	2.1
n (moles gas/kg)	35.1	36.6	—	35.9	39.7
Q	865	780	—	870	660
C_v	0.317	0.304	—	0.332	0.303
T_2	3000	2830	—	3340 (T_2)	2280

TABLE V. Explosion properties of various types by fugacity and partial pressure methods.
(a = fugacity method; b = partial pressure method.)

Products	PETN (density = 1.6)		Cyclonite (1.6)		LNG (1.6)		Tetryl (1.6)		60% St. Dyn. (1.32)	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
CO (moles/kg)	4.7	6.5	8.0	10.1	1.1	2.6	10.6	18.1	6.7	7.0
CO ₂	11.1	9.3	5.5	3.4	12.1	10.6	6.6	2.9	8.3	8.0
H ₂	0.5	0.9	1.3	3.5	0.1	0.3	0.5	2.9	0.9	1.1
H ₂ O	10.9	11.2	8.0	9.8	10.8	10.2	2.2	4.0	10.0	10.1
N ₂	5.9	6.1	12.1	13.5	6.4	6.0	7.0	7.0	4.9	4.9
OH	0.1	0.6	—	0.3	0.2	0.9	—	—	—	0.1
NO	0.1	0.5	—	—	0.5	1.2	—	—	0.01	0.02
O ₂	—	0.2	—	—	1.4	1.4	—	—	—	—
Na ₂ O	—	—	—	—	—	—	—	—	1.11	1.11
SO ₂	—	—	—	—	—	—	—	—	—	—
CaO	—	—	—	—	—	—	—	—	0.16	0.16
CH ₄	—	—	—	—	—	—	1.6	0.1	—	—
NH ₃	0.8	—	2.8	—	—	—	0.9	—	0.3	—
HCN	—	—	—	—	—	—	2.9	3.4	—	—
C	—	—	—	—	—	—	2.7	—	—	—
<i>n</i>	34.1	35.4	37.7	40.7	32.6	33.3	32.3	38.3	31.1	32.3
<i>Q</i>	1420	1310	1315	1250	1420	1240	1013	910	985	975
<i>T₃</i>	4770	4420	4530	4330	4780	4350	3650	3470	3690	3590

remaining may be considered to go to free carbon. This calculation is necessarily approximate in view of the absence of heat data for other possible products of detonation involving carbon.

RESULTS

Table IV presents calculated results for TNT at densities of 1.59 g/cc (cast) and 1.0 g/cc for (A) "adiabatic" or "explosion" conditions, and (B) for conditions occurring at the Chapman-Jouguet plane. Also included in Table IV are experimental results obtained by Haid and Schmidt¹⁴ in a method designed to "freeze" the equilibrium corresponding to the "explosion" state. A careful examination of the comparative results between experimental and calculated data reveals some definite consistencies if one interprets the experimental data on the basis that the experimental method does not entirely "freeze" the equilibria at those corresponding to "explosion" state. The excellent agreement in CO is probably not fortuitous; this type of agreement is quite general as has been found in numerous other comparisons by the author of calculated and experimental data. In fact, one has theoretical justification for the consideration that a moderate shift in the water gas equilibrium from

the "explosion" state (by decreasing *T*) should not affect the CO concentration appreciably when CH₄ and HCN are present in the gas mixture. The failure to freeze the water gas equilibrium completely is reflected, however, in low CO₂ and high H₂O in the experimental data. CH₄ will exist in relatively large amounts only because the pressure is very high. One would expect the pressure to drop more rapidly than the temperature, after detonation, because of the co-volume effect, so that CH₄ would tend to decompose into C and H₂. HCN would tend to decompose as the temperature decreases. Both effects would result in high C and H₂ concentrations as observed. Since NH₃ is very sensitive to H₂ concentrations, one accounts for the excess NH₃ found experimentally on the basis that it formed during the decomposition of CH₄ and HCN.

Table V lists results calculated by the fugacity and partial pressure methods. When the temperature is high and/or the oxygen balance is quite negative the two calculations lead to quite different results. However, as the oxygen balance approaches zero the differences become less, and, if the "explosion" temperature is also low the difference between the partial pressure and the fugacity methods is negligible at or near zero O.B.

¹⁴ A. Haid and A. Schmidt, Zeits. ges. Schiess-Sprengstoffw. 26, 253, 293 (1931).