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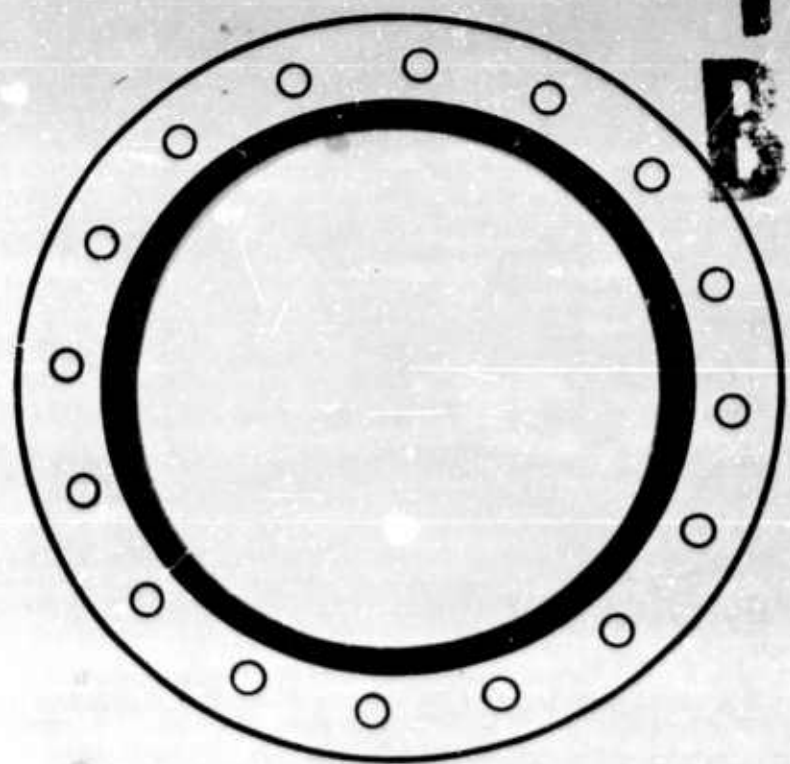
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U. S. NAVAL POWDER FACTORY
RESEARCH AND DEVELOPMENT DEPARTMENT
INDIAN HEAD, MARYLAND

No. 104

15 July 1955

REVISION OF ADDITIVE CONSTANTS
FOR THE SIMPLE CALCULATION OF
THERMOCHEMICAL PROPERTIES
FOR USE IN BALLISTICS

By

B. W. Lewis
S. Goldhagen

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FOREWORD

This revision of thermochemical additive constants and equations for calculating them was performed under Bureau of Ordnance Task Assignment NPF-B2d-02-15-54. It is part of a program to keep methods of calculating thermochemical properties of propellants up to date. Values of constants are published with the reservation that they may be modified by future work and new data in the literature. The data are as of 1 April 1955.

W. C. Cagle
Head, Chemical
Physics Division

Approved by:

Sol Skolnik
Director, Research and
Development Department

Released by:

George E. King
Captain, USNavy
Commanding Officer

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ABSTRACT

The equations for the calculation of the thermochemical additive constants of propellant ingredients, originally presented by Hirschfelder and Sherman in 1942, are revised to accommodate the later thermochemical data of combustion products and ingredients. The new constants, which are for the terms energy released (E), mean heat capacity (C_V), and number of moles of gas (n), were calculated and are tabulated for a number of the most used ingredients. Separate unique consideration is given for potassium sulfate and for basic lead carbonate, resulting in larger differences in constants than are obtained for the generalized treatment of organic ingredients.

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REVISION OF ADDITIVE CONSTANTS FOR THE SIMPLE CALCULATION
OF THERMOCHEMICAL PROPERTIES FOR USE IN BALLISTICS

In 1942 Hirschfelder and Sherman⁽¹⁾ presented a method for the simplified calculation of thermochemical properties for propellants by means of additive constants. Since then there have been a number of changes in the values of the thermochemical data used for these calculations. It is the purpose of this report to tabulate the newer data, to revise the equations for the additive constants on the basis of these data, and to calculate new constants for some of the most used ingredients. The revisions have been made following the procedures given by Hirschfelder and Sherman.⁽¹⁾

DATA

Experimental data were obtained from as many sources as were available to the authors. Reasonable estimates were made when no data could be found. Changes from previous data involved the energy of formation at 0° K of carbon monoxide and carbon dioxide, the heat capacity of graphite and water(g), and correction of molar properties to conform with the latest international atomic weight for carbon, i.e., 12.011.⁽¹⁵⁾ Values for the heat capacities of hydrogen, nitrogen, carbon dioxide, and carbon monoxide had also changed slightly. The

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data used for the calculation of the equations for the constants are given in Table I. The thermochemical and molecular data for ingredients are given in Table II. The atomic composition data for ingredients are given in Table III.

REVISED EQUATIONS

The revised equations for the calculation of the additive constants E_i and C_{v_i} are as follows:

$$E_i = E(1)_i - 38966C_i - 6252H_i + 52073O_i - 6721N_i$$

$$C_{v_i} = 1803C_i + 3.264H_i + 5.008O_i + 3.382N_i$$

For E_i an alternative equation may be used

$$E_i = H.C. - 133018C_i - 40019H_i + 52073O_i - 6721N_i$$

The equation for n_i remains the same, i.e.,

$$n_i = C_i + 1/2H_i + 1/2N_i$$

E_i , C_{v_i} , and n_i are the additive constants for energy released, mean heat capacity, and number of moles of gas for ingredient i , respectively. C_i , H_i , O_i , and N_i are the number of gram-atoms of the elements per gram of ingredient i . $E(1)_i$ is the negative of the energy of formation at 15° C (288.16° K) of the ingredient in cal/gram i.e., $\frac{\Delta E_f(15^\circ C)}{M}$ where ΔE is the molar quantity and M is the molecular weight. H. C. is the heat of combustion of the ingredient in calories per gram at 15° C for liquid-water product and constant volume. These equations are only changed in the values of the

Table I
THERMOCHEMICAL DATA FOR COMBUSTION PRODUCTS OF PROPELLANT INGREDIENTS

| Product | \bar{C}_{p15}° -25° C Cal/deg-mole | \bar{C}_{v15}° -25° C Cal/deg-mole | ΔE_{f15}° C Kcal/mole | $E_{288.16}^{\circ}$ K - E_0° Cal/mole | ΔE_{f0}° K Kcal/mole | E_{2500}° K - E_0° Cal/mole | $\bar{C}_{v2000-3000}^{\circ}$ K Cal/deg-mole |
|----------------------------------|--|--|---|--|--|--|--|
| C (graphite) ^a | 2.021 | 2.021 | 0 | 231.4 | 0 | --- | --- |
| H ₂ (g) | 6.879 | 4.892 | 0 | 1382.1 | 0 | 13856 | 6.527 |
| O ₂ (g) | 7.013 | 5.026 | 0 | 1426.5 | 0 | 15835 | 7.309 |
| N ₂ (g) | 6.960 | 4.973 | 0 | 1430.1 | 0 | 14872 | 5.763 |
| CO (g) ^a | 6.965 | --- | --- | --- | -27.2029 | 15041 | 6.811 |
| CO ₂ (g) ^a | 8.820 | --- | -94.0518 | --- | -93.9707 | 26515 | 12.812 |
| H ₂ O (g) | 8.022 | --- | --- | --- | -57.1040 | 20806 | 10.542 |
| H ₂ O (liq) | 18.010 | --- | -67.5347 | --- | --- | --- | --- |
| Calc'd. from data of Ref. | (13) | (13) | (12) | (8) | (12) | (8) | (8) |

^a All data corrected to latest value of atomic weight for carbon, 12.011(15).
 Notation: \bar{C}_{p15}° -25° C and \bar{C}_{v15}° -25° C are the mean molar heat capacities at constant pressure and volume, respectively, between the indicated temperatures; ΔE_{f15}° C is the energy of formation at 15° C; $E_{288.16}^{\circ}$ K - E_0° is the energy to heat from 0° K to 288.16° K; ΔE_{f0}° K is the energy of formation at 0° K; E_{2500}° K - E_0° is the energy to heat from 0° K to 2500° K; $\bar{C}_{v2000-3000}^{\circ}$ K is the mean heat capacity at constant volume in the range of 2000° - 3000° K.

Table II
THERMOCHEMICAL AND MOLECULAR DATA FOR SELECTED PROPELLANT INGREDIENTS

| Ingredient | Formula | Formula weight | Heat of formation | | Energy of formation $\Delta H_f 15^\circ \text{C}$ Kcal/mole | $\bar{H}(1)$ Cal/gram | $\bar{C}_p 15^\circ-25^\circ \text{C}$ | |
|---------------------|--|----------------|---|-------|--|--------------------------|--|------|
| | | | $\Delta H_f 25^\circ \text{C}$ Kcal/mole | Ref | | | Cal/deg-mole | Ref |
| Butyl stearate | $\text{C}_{22}\text{H}_{44}\text{O}_2$ | 340.594 | -253.92E/ | | -240.715 | 706.8 | 153.3E/ | |
| Dibutyl phthalate | $\text{C}_{16}\text{H}_{22}\text{O}_4$ | 278.352 | -204.15 | (11) | -196.378 | 705.5 | 89.243 | (11) |
| Dioctyl phthalate | $\text{C}_{24}\text{H}_{38}\text{O}_4$ | 390.568 | -258.88E/ | | -246.665 | 631.6 | 175.8E/ | |
| Diphenylamine | $\text{C}_{12}\text{H}_{11}\text{N}$ | 169.228 | 30.624E/ | (3,7) | 34.146 | -201.8 | 57.03 | (10) |
| Ethyl alcohol | $\text{C}_2\text{H}_6\text{O}$ | 46.070 | -66.356 | (12) | -64.337 | 1396.5 | 26.64 | (12) |
| Ethyl centralite | $\text{C}_{17}\text{H}_{20}\text{O}_2$ | 268.363 | -31.27 | (11) | -24.612 | 91.7 | 106.327 | (11) |
| Nitrocellulose, 50% | | | | | | | | |
| " | | 250.755 | | | -175.804 | 701.1 | | |
| " | | 257.141 | | | -172.259 | 669.9 | | |
| " | | 263.865 | | | -168.594 | 638.7 | | |

See footnotes at end of table

Table II (cont'd)

| Ingredient | Formula | Formula weight | Heat of formation | | Energy of formation ΔE_f^0 Kcal/mole | E(l) Cal/gram | \bar{C}_p 15° - 25° C/ Cal/deg-mole | | Ref |
|---------------------------------|-------------------------|----------------|----------------------------------|--------------------|--|------------------|--|--------------|------|
| | | | ΔH_f^0 Kcal/mole | 25° C Kcal/mole | | | 15° C Kcal/mole | Cal/deg-mole | |
| Nitrocellulose, %N _d | | | | | | | | | |
| " | 12.20 | 266.650 | | | -167.003 | 626.3 | | | |
| " | 12.60 | 272.404 | | | -163.853 | 601.5 | | | |
| " | 12.80 | 275.380 | | | -162.089 | 588.6 | | | |
| " | 13.00 | 278.418 | | | -160.424 | 576.2 | | | |
| " | 13.15 | 280.740 | | | -159.123 | 566.8 | | | |
| " | 13.25 | 282.310 | | | -158.207 | 560.4 | | | |
| " | 13.50 | 286.315 | | | -155.899 | 544.5 | | | |
| " | 14.14 | 297.101 | | | -149.858 | 504.4 | | | |
| 2-Nitrodiphenylamine | <chem>C12H10O2N2</chem> | 214.228 | 17.819 ^E | | 21.911 | -102.3 | 64.268 ^E | | |
| Nitroglycerin | <chem>C3H5O9N3</chem> | 227.097 | -89.123 ^E | | -84.285 | 371.1 | 68.13 ^E | | |
| Nitroguanidine | <chem>CH4O2N4</chem> | 104.075 | -22.14 ^b ^E | (12) | -19.260 | 185.1 | 35.014 | | (11) |

See footnotes at end of table.

Table II (cont'd)

| Ingredient | Formula | Formula weight | Heat of formation | | Energy of formation ΔE_f 15° C/ Kcal/mole | E(1) Cal/gram | \bar{C}_p 15°-25° C/ Cal/deg-mole | Ref |
|----------------------|--------------------------|----------------|---------------------------------|------|---|------------------|--|-----|
| | | | ΔH_f 25° C Kcal/mole | Ref | | | | |
| Petroleumium | $C_{20}H_{42}$ | 282.556 | -152.706 | (13) | -120.247 | 425.6 | 141.3 ^c | |
| RDX | $C_3H_6O_6N_6$ | 222.129 | +19.093 | (9) | 24.266 | -109.2 | 66.64 ^c | |
| Water (liq) | H_2O | 18.016 | -68.3174 | (12) | -67.5347 | 3748.6 | 18.010 | (3) |
| Basic lead carbonate | $2PbCO_3 \cdot Pb(OH)_2$ | 775.668 | -435.4 ^c | (14) | -431.057 | 557.5 | 50.2 ^c | |
| Potassium sulfate | K_2SO_4 | 174.266 | -342.66 | (12) | -341.491 | 1959.6 | 30.835 | (6) |

^a/Corrected for lattice energy weight of carbon 12.011 (15)

^b/Mean of two values.

^c/Estimated by authors to be reasonable value.

^d/Thermochemical data for calculations of nitrocellulose constants were obtained from ref (4) and an assumed specific heat value of 0.36 cal/gram. Values for other percentage nitrogen nitrocelluloses may be obtained by linear interpolation.

^e/Calculated from $\Delta H_f^{25^\circ C}$. The number of significant figures in table is not an indication of the accuracy of the data but is used here for consistency.

^f/These values of \bar{C}_p were used to calculate $\Delta H_f^{15^\circ C}$ from $\Delta H_f^{25^\circ C}$.

^g/Experimentally determined in these laboratories.

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Table III
 GRAM-ATOMIC WEIGHTS OF ELEMENTAL CONSTITUENTS PER GRAM OF INGREDIENT
 FOR SELECTED PROPELLANT COMPOUNDS

| Compound | Gram-atomic weights/gram | | | |
|-----------------------------|--------------------------|----------------|----------------|----------------|
| | C ₁ | H ₁ | O ₁ | N ₁ |
| Butyl stearate | .064593 | .129186 | .005872 | .000000 |
| Dibutyl phthalate | .057481 | .07037 | .014370 | .000000 |
| Dioctyl phthalate | .061449 | .097294 | .010241 | .000000 |
| Diphenylamine | .070910 | .065001 | .000000 | .005909 |
| Ethyl alcohol | .043412 | .130236 | .021706 | .000000 |
| Ethyl centralite | .063347 | .074526 | .003726 | .007453 |
| Nitrocellulose ^a | .023928 | .032027 | .035645 | .007853 |
| " | .023333 | .030680 | .035864 | .008210 |
| " | .022739 | .029332 | .036082 | .008567 |
| " | .022501 | .028793 | .036170 | .008709 |
| " | .022026 | .027715 | .036345 | .008995 |
| " | .021788 | .027176 | .036432 | .009138 |

^a See footnote at end of table

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Table III (cont'd)

| Ingredient | Gram-atomic weights/gram | | | |
|---------------------------------------|--------------------------|----------------|----------------|----------------|
| | C ₁ | H ₁ | O ₁ | N ₁ |
| Nitrocellulose ^{a/} 13.00% N | .021550 | .026637 | .036519 | .009280 |
| " 13.15% N | .021372 | .026233 | .036585 | .009387 |
| " 13.25% N | .021555 | .025965 | .036624 | .009459 |
| " 13.50% N | .020956 | .025289 | .036738 | .009637 |
| " 14.14% N | .020195 | .023564 | .037018 | .010094 |
| 2-Nitrodiphenylamine | .056015 | .046679 | .009336 | .009336 |
| Nitroglycerin | .013210 | .022017 | .039631 | .013210 |
| Nitroguanidine | .009608 | .038434 | .019217 | .038434 |
| Petrolatum | .070782 | .148643 | .000000 | .000000 |
| LDX | .013506 | .027011 | .027011 | .027011 |
| Water (liq) | .000000 | .111012 | .055506 | .000000 |
| Basic lead carbonate | .002578 | .002578 | .010314 | .003868 |
| Potassium sulfate | .011477 | .000000 | .022953 | .005738 |

^{a/} Intermediate values for different percentage nitrogen of nitrocelluloses may be obtained by a linear interpolation.

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numerical coefficients and have been arrived at by adherence to the methods and procedures of Hirschfelder and Sherman.⁽¹⁾

CALCULATED ADDITIVE CONSTANTS FOR SELECTED PROPELLANT INGREDIENTS

The additive constants E_i , C_{v_i} , and n_i have been calculated from the above equations for a number of the most common propellant ingredients and are given in Table IV. Numerous changes in energy of formation of ingredients including the nitrocelluloses were noted. For the inorganic salts, basic lead carbonate and potassium sulfate, the calculations had to be made by considering the effects of these ingredients to be unique. The calculations of the constants for these salts are given in Appendix A.

USE OF ADDITIVE CONSTANTS

The adiabatic flame temperature and impetus of a propellant are calculated by means of equations given by Hirschfelder and Sherman.⁽²⁾ These equations are:

$$T_0 = 2500 + \frac{\sum x_i E_i}{\sum x_i C_{v_i}}$$

and

$$I = \sum x_i n_i RT_0$$

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Table IV

THERMOCHEMICAL ADDITIVE CONSTANTS FOR PROPELLANT INGREDIENTS

| Compound | | E_1 | C_{v1} | n_1 |
|------------------------------|----------|---------|----------|-----------------------|
| Butyl stearate | | -3726. | .5675 | .12919 |
| Dibutyl phthalate | | -2691. | .4336 | .09700 |
| Diocetyl phthalate | | -3101. | .4796 | .11010 |
| Diphenylamine | | -3007. | .3600 | .10636 |
| Ethyl alcohol | | -2772. | .6121 | .10853 |
| Ethyl centralite | | -2882. | .4013 | .10434 |
| Nitrocellulose ^{a/} | 11.00% N | -30.4 | .3528 | .04387 |
| " | 11.50% N | 41.5 | .3496 | .04278 |
| " | 12.00% N | 113.2 | .3464 | .04169 |
| " | 12.20% N | 141.9 | .3451 | .04125 |
| " | 12.60% N | 199.1 | .3426 | .04038 |
| " | 12.80% N | 228.2 | .3413 | .03994 |
| " | 13.00% N | 256.8 | .3401 | .03951 |
| " | 13.15% N | 278.4 | .3391 | .03918 |
| " | 13.25% N | 293.0 | .3385 | .03896 |
| " | 13.50% N | 329.1 | .3369 | .03842 |
| " | 14.14% N | 421.2 | .3328 | .03702 |
| 2-Nitrodiphenylamine | | -1949. | .3317 | .08402 |
| Nitroglycerin | | 951.5 | .3388 | .03082 |
| Nitroguanidine | | -57.4 | .3690 | .04804 |
| Petrolatum | | -4113. | .6128 | .14510 |
| RDX | | 639.0 | .3391 | .04052 |
| Water(liq) | | -1552.2 | .6403 | .05551 |
| Basic lead carbonate | | -199.7 | .0910 | .00387 |
| Potassium sulfate | | -1226.5 | .2708 | -.00574 ^{b/} |

^{a/} Intermediate values for other percentage nitrogen nitrocelluloses may be obtained by linear interpolation.

^{b/} Note that the negative is intentional. See Appendix A for derivation.

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where T_0 is the adiabatic flame temperature in °K, x_i is the weight fraction of the i th ingredient in the propellant, f is the impetus in ft-lb/lb when R the gas constant is 2781.7 ft-lb-gram/deg-lb-mole, and $\sum_i x_i E_i$, $\sum_i x_i C_{v_i}$, and $\sum_i x_i n_i$ are the sums of the product of the weight fraction and the additive constants for all ingredients of the propellant. In connection with the calculation of these ballistic properties it is necessary to know the composition of the propellant including that of the volatiles. Usually the volatiles are determined as a total, and one must estimate what they are composed of and in what weight ratio. Knowledge of the type of powder and its manufacture may give one a basis for the estimation. The conventions used by the authors, based on experience with ether-alcohol solvent-extruded propellants, are given in Appendix B.

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APPENDIX A

CALCULATION OF THE ADDITIVE CONSTANTS FOR BASIC LEAD
CARBONATE AND POTASSIUM SULFATEBasic Lead Carbonate, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$

Basic lead carbonate was considered to contribute to the water-gas equilibrium and to contribute liquid metallic lead in the form of fine droplets. Examination of the critical temperature and pressure of lead indicated that the most probable state under gun conditions was the liquid. Thus the calculations of E_1 and C_{V1} had to allow for the production and presence of lead.

Calculation of E_1 :

$$E_1 = -E(1) + E(2) + E(3) - E(4)$$

according to Hirschfelder and Sherman.⁽¹⁾ In this case the presence of lead affects only the values of $E(2)$ and $E(4)$. $E(1)$ was estimated to be 557.5 cal/gram from the data for heat of reaction given in reference (14).

$E(2)$ is the energy involved when the elements present are cooled from 288.16° to 0° K. The contribution of the lead in this compound to $E(2)$ was estimated to be 5.49 cal/gram.

$E(4)$ is the energy necessary to heat the product gases (and/or finely divided liquids and solids) from 0° to 2500° K. The contribution of lead in this compound to $E(4)$ was estimated to be 68.2 cal/gram, and the contribution to $E(2) - E(4)$ was

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-62.7 cal/gram for the lead in this compound. This figure was then added to the value of E_1 obtained for this compound on the basis of the regular E_1 equation. Thus:

$$E_1 = -E(1) = 38966C_1 + 6252H_1 + 52073O_1 - 62.7 = 199.7 \text{ cal/gram.}$$

Calculation of C_{V1} :

The assumption was made that the fine droplets of liquid lead were in thermal equilibrium with the gas and therefore a term for lead had to be added to the C_{V1} equation. Thus:

$$\begin{aligned} C_{V1} &= 1.803C_1 + 3.264H_1 + 5.008O_1 + 6.10 \text{ Pb}_1 \\ &= .09102 \text{ cal/degree-gram.} \end{aligned}$$

Calculation of n_1 :

The fine droplets of lead were not considered to contribute to the number of moles of gas per gram. Thus:

$$\begin{aligned} n_1 &= C_1 + 1/2H_1 \\ &= .003867 \text{ moles/gram.} \end{aligned}$$

The data used in the above calculations are listed in the various tables of this report.

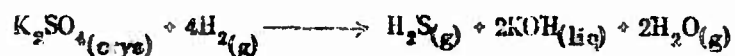
Potassium Sulfate, K_2SO_4

The constants were previously estimated by Hirschfelder and Sherman⁽²⁾ on the assumption that, in guns, potassium sulfate vaporizes as potassium sulfate molecules. It was felt that this treatment was not a realistic one when reducing gases were present. A qualitative study was made of the products of explosion of a powder containing 4% potassium sulfate. This

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powder was fired in a calorimetric bomb, and the gases were found to contain a considerable quantity of hydrogen sulfide. The residue left in the bomb was dissolved in water and tested for the presence of sulfate ion. This test showed a negligible amount of sulfate present. From this experiment it was felt that a more accurate estimate of the reaction of potassium sulfate in a propellant was:



The hydrogen would be furnished by the water-gas equilibrium, which would adjust itself to the required condition. The calculations were made on the basis of the above assumptions with the additional products taken into consideration.

Calculation of E₁:

E(1), the negative of the energy of formation per gram, was calculated in a straight-forward manner from the heat of formation and was found to be 1959.6 cal/gram.

E(2), the energy to lower the temperature of the elements from 288.16° to 0° K, was calculated from the usual type equation.

$$\begin{aligned} E(2) &= 1630\text{K}_2 + 1291\text{S}_8 + 7130\text{O}_2 \\ &= 425 \text{ cal/gram.} \end{aligned}$$

E(3) is the energy of formation of the combustion products.

Equations for E(3) were obtained for the two extreme cases:

(a) no carbon dioxide formed and (b) no water formed. These

cases followed the method of Hirschfelder and Sherman⁽¹⁾ but included the $K_2SO_4 + 4H_2$ reaction. This inclusion was made by considering the reaction to be:



Then the equations relating the number of moles of products to the gram-atoms of elements of the reactants were as follows:

$$n_{CO_2} = 4S - 1/2H + O - C + n_{H_2}$$

$$n_{CO} = 2C - O + 1/2H - 4S - n_{H_2}$$

$$n_{H_2O} = 1/2H - 2S - n_{H_2}$$

$$n_{N_2} = 1/2N$$

$$n_{KOH} = K - 2S$$

$$n_{H_2S} = S$$

$$n_{H_2} = n_{H_2}$$

where the n's are in moles per gram and the C, H, O, N, K, and S are in gram-atoms per gram of the elements in the powder. Thus for the two cases:

(a) when $n_{CO_2} = 0$

$$n_{H_2} = C + 1/2H - O - 4S$$

$$n_{CO} = C$$

$$n_{H_2O} = O - C + 2S$$

(b) when $n_{H_2O} = 0$

$$n_{H_2} = 1/2H - 2S$$

$$n_{CO_2} = O - C + 2S$$

$$n_{CO} = 2C - O - 2S$$

The other concentration expressions remained the same in both cases. The values for the separate cases were each substituted into the E(3) expression;

$$E(3) = (n\theta)H_2O + (n\theta)CO_2 + (n\theta)CO + (n\theta)H_2S + (n\theta)KOH$$

where θ is the energy of formation at 0° K of the various product compounds as given in Table I and Table V. Thus two expressions were obtained, E(3)^a and E(3)^b in terms of constants and gram-atoms per gram of elements.

Table V
THERMOCHEMICAL DATA FOR SELECTED SUBSTANCES

| Substance | \bar{C}_v , Cal/deg-mole | | ΔE , Kcal/mole | |
|---------------------|----------------------------|---------------------|------------------------|----------------------|
| | 0°-288.16° K | 2000°-3000° K | Formation 0° K | 0°-2500° K |
| K(crys) | 5.657 ^{a/} | --- | 0 | --- |
| S(rh) | 4.480 ^{b/} | --- | 0 | --- |
| H ₂ S(g) | --- | 14.23 ^{c/} | 4.123 ^{a/} | 21.825 ^{b/} |
| KOH | --- | 18.0 ^{c/} | 102.376 ^{c/} | 49.440 ^{c/} |

^{a/} Reference (13)

^{b/} Reference (5)

^{c/} Authors estimate

E(4) is the energy to heat all the products from 0° to 2500° K. E(4) equations were obtained for the two cases in a manner quite similar to that for E(3) from the equation:

$$E(4) = (na)H_2O + (na)H_2 + (na)CO_2 + (na)CO + (na)H_2S + (na)KOH + (na)N_2$$

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where the α 's are the energy to heat the respective products from 0° to 2500° K. Thus $E(4)^a$ and $E(4)^b$ expressions were obtained.

According to Hirschfelder and Sherman⁽¹⁾:

$$E(3) = 0.77E(3)^a + 0.23E(3)^b$$

and

$$E(4) = 0.77E(4)^a + 0.23E(4)^b$$

and thus

$$E(3) - E(4) = 0.77(E(3)^a - E(4)^a) + 0.23(E(3)^b - E(4)^b)$$

A expression was derived from this for $E(3) - E(4)$ in terms of constants and the gram-atoms per gram of elements. A similar $E(3) - E(4)$ expression was obtained for the CHON system alone, and this expression was subtracted from that for the CHON plus potassium sulfate to give an expression for the potassium sulfate alone. Thus the expression:

$$(E(3) - E(4))_1 = .77K_1\Phi_{H_2O} + (S_1 + .27K_1)\Phi_{H_2} - .23K_1\Phi_{CO_2} + .23K_1\Phi_{CO} + S_1\Phi_{H_2S} + K_1\Phi_{KOH}$$

was obtained, where $\Phi = \Delta E_{T_0}^\circ K - \Delta E_{2500}^\circ 0^\circ K$

for the various products. Substituting the numerical values gave:

$$(E(3) - E(4))_1 = 120348S_1 \\ = 690.6 \text{ cal/gram}$$

combining $-E(1) + E(2) + E(3) - E(4)$ gave:

$$E_1 = -1226.5 \text{ cal/gram}$$

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Calculation of C_{v1} :

An expression for C_{v1} was obtained from

$$C_v = (nC_v)_{H_2O} + (nC_v)_{H_2} + (nC_v)_{CO_2} + (nC_v)_{CO} + (nC_v)_{H_2S} + (nC_v)_{KOH} + (nC_v)_{N_2}$$

together with the same concentration expressions and the two extreme cases: (a) no carbon dioxide and (b) no water. Expressions were obtained for C_v^a and C_v^b for both the CHONKS and CHON systems and the difference was obtained. Both C_v^a and C_v^b were given equal weight in obtaining the final expression, i.e.,

$$C_{v_1} = 1/2 [C_v^a + C_v^b]$$

The resultant equation was:

$$C_{v_1} = 47.192S_p \\ = 0.27079 \text{ cal/deg-gram}$$

Calculation of n_1 :

On the basis of the reaction that was assumed between potassium sulfate and hydrogen, it was seen that the net effect was the consumption of 1 mole of gas rather than the furnishing of gas. Thus the value of n_1 had to be negative, and

$$n_1 = -S_p \\ = -.005738 \text{ moles/gram}$$

APPENDIX B

CONVENTIONS USED AT NPF FOR THE ESTIMATION OF THE COMPOSITION
OF TOTAL VOLATILES IN CONVENTIONAL GUN PROPELLANTS
USING ETHER-ALCOHOL SOLVENTLow Total Volatiles

When total volatiles are 0.7% or less, the volatiles are considered to be only water. This convention covers most nitroguanidine and most RDX powders that are solvent extruded.

High Total Volatiles

When the propellant has a high total-volatile content, the volatiles are considered to consist of 0.7% water, and the remainder is considered to be ethyl alcohol. This convention covers single- and double-base solvent-extruded powders.

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