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Thermochemical Data for Propellant Ingredients and their Products of Explosion

H. H. M. Pike

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(Theoretical Research Report No. 4/49)

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H.H.M. Pike

Summary

The tables published by the same author in 1940 have been revised and extended. The data on the gaseous products have been modified to provide a consistent set based on recently determined values of the fundamental constants and the figures for H_2O and CO_2 have been completely recalculated from more recent spectroscopic data. A table of entropies has been added, for use in rocket calculations. The list of propellant ingredients has been extended to include some liquid propellants and a few high explosives. Finally, differences between British and American thermal data for nitrocellulose have been shown to be real and to agree with the differences of 0.1% in estimated nitrogen contents pointed out by Raff and McHenry.

A short account of the use of the tables is included together with the application of Corner's corrections for the non-ideal state of the gas at gun pressures. Finally, two examples of the methods of calculation are given.

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Introduction

The tables originally published by the author(1) in 1940 were collected from many sources and had quite a wide distribution in this country owing to their convenience. A similar set of tables was published independently by Hirschfelder et al. in America(2). These authors included corrections for departures from ideal gas conditions at the pressures obtaining in guns but such corrections have been published independently by Corner(3) in this country and so are not reproduced here. The properties of the gaseous products have been tabulated at 100° intervals and smoothed to facilitate interpolation. Calculations of adiabatic expansions are considerably simplified by the use of a table of entropies and so this has been included. A table of free energies is also given so that equilibrium constants can be calculated for other reactions than those treated here.

Information on sulphur, potassium and chlorine compounds is available in the open literature and this has been collected, amplified where necessary and systematised in a GALCIT Report published by Altman(4). An independent report by Luft(5) also includes fluorine. Consequently no information on these compounds has been included in the present report.

Some of the data for the product gases have been interpolated from that published by Wagman et al.(6), some has been obtained by modifying older published material and for CO_2 and H_2O completely new calculations from spectroscopic data have been carried out. Full details are given in the appropriate section.

A considerable amount of information on heats of combustion or calorimetric values of propellant ingredients has been made available in the last nine years and this has been used in compiling Table 1. In all cases care has been taken to give as accurate a value of the calorimetric value as possible since this is very nearly equal to the heat liberated in a propellant explosion. The cal.val. (water liquid) is a very convenient quantity to tabulate since it is independent, to within 1 cal./gm., of the value of the water gas equilibrium constant. It is also nearly independent of the temperature at which the measurement is carried out, the variation being of the order of -1 cal./gm. per 15°C increase in temperature.

Corrections to cal.val. determinations have been discussed in a previous paper(7). For convenience in thermochemical calculations the standard end state has been taken to be CO_2, CO, H_2, N_2 and water, all under a pressure of one atmosphere. Published values of cal.vals. have usually been corrected for the formation of byproducts but not for the fact that the final cooled products are at quite a high pressure. To correct to one atmosphere pressure we must subtract a quantity proportional to the density of loading and amounting to about 5 cal./gm. for a density of loading of 1 gm. of explosive per 10 c.c. bomb volume, this correction varying slightly with composition of the explosive. The cal.vals. given in this report have also been corrected to a temperature of 300°K. The heats of formation and combustion in Table 1 are related to the cal.vals. by the formulae

$$\text{H.F.} = 67380\,(\text{O}) - 40670\,(\text{C}) - \text{Cal.val.} \qquad (1)$$

$$\text{H.C.} = 134720\,(\text{C}) + 33705\,(\text{H}) - 67380\,(\text{O}) + \text{Cal.val.} \qquad (2)$$

these figures corresponding to heats of combustion at constant volume at 300°K of 94050, 67410 and 67340 cal./mole for C, H_2 and CO. The corresponding H.F. of steam at constant volume at 300°K is 57500 cal./mole. These are conventional formulae derived as follows - we assume $(\text{O}) > (\text{C})$ so that we have no free carbon but $2\,(\text{C}) + \frac{1}{2}\,(\text{H}) > (\text{O})$ so that we have some H_2 and CO. If no CO_2 were formed we should have

$$\text{Cal.val.} = 26710\,(\text{C}) + 67410\,\{(\text{O}) - (\text{C})\} - \text{H.F.}$$

while if no H_2O were formed we should have

$$\text{Cal.val.} = 26710\,(\text{C}) + 67340\,\{(\text{O}) - (\text{C})\} - \text{H.F.}$$

Actually we get rather more H_2O than CO_2 from propellants. If we assume the ratio of the two amounts to be 4 : 3 then our formula is exact, but the error is always less than 1 cal./gm.

It should be noted that we take the elementary form of carbon to be graphite, the other elements being, of course, gaseous.

The cal.vals. of non-explosive materials such as carbamite are their effective values when small quantities are added to a propellant and in many cases are negative. It is assumed that the heat of mixing of propellant ingredients is negligible.

1. Heats of formation of propellant constituents.

(a) Nitrocellulose. The original tables gave figures based on the mean values of the heats of combustion given by Prettre(8) and by Schmidt and Becker(9). In each case samples were burnt at constant volume in a bomb initially filled with oxygen to about 30 atmospheres pressure. Schmidt and Becker used the Lunge method for estimating the nitrogen content of the N.C. but Prettre's method is not stated. Schmidt and Becker corrected for the formation of nitric acid in the bomb and other heat corrections are negligible. Apparently they did not correct for chalk in the nitrocellulose which might amount to ½%. Such an amount would make the observed heat of combustion too low by 12 cal./gm. and if the CO_2 were liberated in the nitrometer it would add .14% to the measured nitrogen content. Prettre's results are probably subject to the same errors.

The results of both sets of experiments agree quite closely with the direct cal.val. determination of de Bruin and de Pauw(10). The same amount of chalk would here produce an error of only 5 cal./gm. but the actual chalk content must have been less than this since the N.C. was precipitated. These authors used the Schulze-Thiemann method of nitrogen estimation, which according to Schmidt and Becker gives results some .2% lower than those given by the Lunge method. The charges were fired at a density of loading of about .01 gm/c.c. so that corrections for byproducts and final pressure were negligible; the bomb was, however, evacuated to 2 mm. air pressure before firing and so the reaction may have been incomplete.

In the original tables the mean of the values for heats of combustion given by Prettre and by Schmidt and Becker were used without correction and in consequence the cal.val. figures deduced were probably too low. More recent work by Milus(11) gives cal.vals. of N.C. for nitrogen contents varying from 12.62 to 13.45%. The nitrogen contents were determined by the du Pont nitrometer method and so are reasonably accurate, they were reproducible to ± .02% N. No mention is made of chalk or ash content but since the measured gas volumes agreed very closely with the calculated values this must have been very small. The density of loading was 0.1 gm/c.c. and subtracting 5 cal./gm. to bring the results to atmospheric pressure we get by least squares

$$\text{Cal.val.} = -925 + 149.18\,p \qquad (3)$$

where p is the % by weight of nitrogen in the N.C. This fits the observed results within 3 cal./gm.

Similar work has been carried out by Taylor and Hall(12) for four nitrogen contents ranging from 12.1 to 13.24%. In three cases the N.C. was precipitated but in all cases the ash content was measured and allowed for. The density of loading was .04 gm/c.c. and so 2 cal./gm. must be subtracted to correct the cal.vals. to atmospheric pressure. By comparing their tables 9 and 10 we see that methane formation reduced the gas volume by 2.5 or 3 c.cs. The observed cal.vals. were therefore too high by 3 or 4 cal./gm. on this account. A further 1 cal./gm. must be subtracted to correct to a temperature of 27°C, giving final cal.vals. of 1045, 974, 895 and 1054. These are some 8 cal./gm. lower than the figures given in their table 10 for 0°C. Taylor and Hall appear to have increased their cal.val. figures by 5 cal./gm. to correct from 17°C to 0°C whereas we should only add 1 cal./gm. and so it seems that they are in error. Fitting our corrected figures by a least square line we get for the cal.val. at 300°K at atmospheric pressure

$$\text{Cal.val.} = -799 + 140.06\,p \qquad (4)$$

which gives the final figures to within one cal./gm.

Measurements of the heat of combustion of N.C. have also been made by Jessup and Prosen(13). These authors measured the heat of wetting of the nitrocellulose which decreased from 4 cal./gm. for N.C. of 11.5% N content down to 1 cal./gm. for N.C. of 13.4% N content. Correction to atmospheric pressure and correction for nitric acid formed reduced the observed heat of combustion by 3 to 4 cal./gm. The impurity present in the N.C. was not measured directly but deduced from the ratio of the mass of CO_2 formed to the mass calculated for pure N.C., the deduced amount being about 0.3% for N.C. made from cotton and 0.5% for N.C. made from wood pulp. The nitrogen determinations were made by the suppliers of the N.C., the Hercules Powder Company, who presumably used a du Pont nitrometer and, as is customary, gave their nitrogen contents as percentages of the total mass of N.C. plus impurities.

For pure dry N.C. made from either wood or cotton the heat of combustion measurements are fitted with a standard deviation of less than 1 cal./gm. by

$$H.C. = 4179.50 - 140.7187\,p \qquad (5)$$

and so the cal.val. is given by

$$Cal.val. = -806.76 + 139.725\,p \qquad (6)$$

In practice the N.C. will be partly wetted but the heat of wetting will not usually exceed 1 cal./gm. of finished propellant. Also the correction to 27°C from their working temperature of 30°C increases the heat of combustion by less than ½ cal./gm. In using equation (6) we must be careful to use the true nitrogen content of the pure nitrocellulose. For example 1 gm. of dry N.C. made from wood pulp of normal standard of purity and of nominal nitrogen content 12.2% will contain about .995 gms. of pure N.C. of nitrogen content 12.26%. If the impurity is inert, as is usually the case, then the actual cal.val. will be 902 cal./gm. whereas substituting p = 12.2 in equation (6) would give 898 cal./gm.

Equations (3), (4) and (6) give the following values for pure N.C.

p (% N)	11.5	12	12.5	13	13.5
cal.val. (3)	791	865	940	1014	1089
.. .. (4)	812	882	952	1022	1092
.. .. (6)	800	870	940	1010	1080

One would expect Milus' results to be high if he made no correction for chalk and other impurities but the steady difference of 12 cal./gm. between Taylor and Hall's results and those of Jessup and Prosen is well outside the experimental error. If we assume that Jessup and Prosen were given nitrocelluloses whose nitrogen contents were assessed on the pure material then we should have to lower their nitrogen contents and increase their heats of combustion, the nett effect being a reduction of 0.56 cal./gm. in the heat of combustion or cal.val. for a given nitrogen content. Again, any residual solvent would increase the heat of combustion and reduce the cal.val. Taylor and Hall fired their charges in an evacuated bomb and an air leakage of say 5 c.c. per gm. of ppt would not only increase the measured cal.val. by 6 cal./gm. but would also increase the measured gas volume by 4 c.c./gm., and such an increase in gas volume, which would have varied considerably from round to round, was not observed.

The discrepancy can be explained by a systematic difference of about .09 between the percentage nitrogen contents as measured in the U.S. and by I.C.I., the latter obtaining the lower figure. A careful comparison of the two methods by Raff and McHenry(14) showed that the du Pont method, as used in the U.S. gave percentage nitrogen contents consistently higher by .10 than those obtained by the British method. The du Pont method avoids a number of systematic errors that arise in the British method and gives the theoretical figure for inorganic substances. We shall therefore adopt the formula

$$Cal.val. = -810 + 140\,p \qquad (7)$$

which gives the same values as (6) over the range of interest, and make the proviso that for British propellants the stated percentage nitrogen content should be increased by 0.10. Equation (7) gives cal.vals. for pure N.C. 10 to 20 cal./gm.

higher than those in the original tables. The figures for the two types of nitrocellulose commonly used in British propellants with nominal percentage nitrogen contents of 12.2 and 13.15 are 912 and 1045 cal./gm. respectively and these figures combined with those for the other ingredients give a nice fit with measured cal.vals. after correction for byproducts and subtracting the pressure correction.

To avoid confusion we must point out that by British method is meant the routine method used in British propellant factories, which is intended to provide a check on uniformity of production rather than to give absolute values of nitrogen content. A more accurate method is used in E.R.D.E. for special purposes such as the examination of nitrocellulose recovered from propellants.

(b) Nitroglycerine. Schmidt(15) and Rinkenbach(16) gave 1639 and 1630 cal./gm. for the heat of combustion of N.G. at constant volume and in the original tables the mean of these two was taken to give a cal.val. of 1784 cal./gm. More recent work by Burlot(17) gave a heat of combustion of 1623 cal./gm. Unpublished work in the Research Department by Robertson, using mixtures of N.G. and guncotton in a propellant calorimeter gave uncorrected cal.vals. for N.G. alone of 1750 cal./gm. and similar work by Goodwin and Taylor gave mean values of 1770 and 1750. Further unpublished work by Sutton and Ambler in the Research Department in 1932 gave the following results for the cal.val. of N.G.

N.G. plus stick cordite in ppt. bomb	1709
N.G. plus ground	1763
N.G. plus H_2 in heat of combustion bomb	1755
From cal.val. of 60/40 ballistite	1738
From heat of combustion of 60/40 ballistite	1770

The figure adopted by the calorimetric section for calculating the cal.vals. of propellants containing N.G. was 1740 cal./gm. the corresponding figures for N.C. (12.2% N) and guncotton (13.1% N) being 925 and 1040 cal./gm. respectively.

The most recent determinations are heat of combustion measurements by Taylor and Hall(12). Their results for N.G. were not so regular as for N.C., probably on account of oxidation of bomb metal by the excess oxygen. Their best estimate was 1615 cal./gm. for heat of combustion which gives 1761 cal./gm. for the cal.val., corrected to atmospheric pressure. Their corresponding figure obtained by firing propellant mixtures was 1750 cal./gm. Since the combination of N.G. and N.C. in a gelatinised propellant is probably slightly exothermic, the effective value of the cal.val. of N.G. will be a little less than 1761 cal./gm. We shall therefore assume that in gelatinised propellants the effective cal.val. of N.G. is 1750 cal./gm.

(c) Diethylene glycol dinitrate. The heat of combustion reported by Rinkenbach(18) was 2798 cal./gm. at constant volume, giving a cal.val. of 1080 cal./gm. Direct measurement of the cal.vals. of nitromethane and a 60/40 nitromethane/D.G.N. mixture gave figures of 1121 and 1079 cal./gm. respectively. The heat of mixing was -1 cal./gm. giving 1051 cal./gm. for the cal.val. of pure D.G.N. and we shall adopt this value.

(d) Dinitroglycol. Rinkenbach(16) gives 1764 cal./gm. for the heat of combustion, which equals the cal.val. for this substance. The heat of combustion given by Tomioka and Takahashi(19) is 1749 cal./gm. The cal.val. of a 65/35 mixture of D.N.G./nitropropane was determined in the A.R.D. to be 1021 cal./gm. giving a cal.val. for D.N.G. of 1730 cal./gm. and we take 1740 cal./gm. as a weighted mean.

(e) Nitroguanidine, guanidine nitrate and oxamide. Schmidt(15) quotes Matignon's figures of 2032 and 1715 cal./gm. for heats of combustion(19) of the first two, leading to cal.vals. of 737 and 610 cal./gm. respectively. The figure for picrite used in the A.R.D. calorimetric section is 715 cal./gm. Other heats of combustion quoted by Landolt Bornstein (e.g. III c) for picrite are 2010 cal./gm. by Tomioka and Takahashi and 2018 cal./gm. by Badoche.

Some very precise measurements of the heat of combustion of Welland picrite were carried out by Prosen and Gilmont(20) who obtained 2014 cal./gm. Two other samples fired by Stegeman(21) gave heats of combustion of 2002 and 2008 cal./gm.

respectively. The mass of CO_2 formed in Prosen and Gilmont's experiments was 99.96% of that calculated for pure picrite but the actual purity of the sample was not known. The wartime specification for bulk production allowed about 1% of impurities. If we assume that the only impurity in Prosen and Gilmont's sample was .04% of inert matter then the calculated cal.val. is 720 cal./gm. For picrite of normal purity it would be better to take a cal.val. of 715 cal./gm. and this we have done.

No other information appears to be available for guanidine nitrate and so we shall assume a cal.val. of 610 cal./gm. The only available figure for oxamide is a heat of combustion of 2316 cal./gm. given by Stohmann and Hausmann(22) giving a cal.val. of -745 cal./gm.

(f) Dinitrotoluene and Trinitrotoluene. Schmidt(15) gives 4709 and 3599 cal./gm. for the heats of combustion. Prosen and Gilmont(20) were supplied with D.N.T. by the Hercules Powder Company which produced 99.99% of the calculated mass of CO_2 on combustion, with a heat of combustion of 4658 cal./gm. Stegeman(21) found a heat of combustion of 3594 cal./gm. from a practice firing of T.N.T. of unknown purity. Heats of combustion of D.N.T. and T.N.T. quoted by Tomioka and Takahashi are 4691 and 3592 cal./gm. while Burlot(17) gives 4660 and 3596 cal./gm. respectively. Since in recent years only T.N.T. of Grade 1 purity has been used old figures are probably not reliable. Garner and Abernethy(22) measured the heats of combustion of all the isomeric forms of mono-, di- and trinitrotoluene, their figures for 2:4 D.N.T. and 2:4:6 T.N.T. being 4691 and 3623 cal./gm. Their figures ranged from 4691 to 4730 and from 3623 to 3677 cal./gm. for the various isomers.

Prosen and Gilmont's and Garner and Abernethy's heats of combustion of D.N.T. give cal.vals. of -150 and -117 respectively. The figure determined by Taylor and Hall from the cal.val. of propellant mixtures was -135 cal./gm. corrected to atmospheric pressure and we shall adopt this figure. A figure of -180 cal./gm. used in the A.R.D. calorimetric section seems to be too large. Garner and Abernethy's figure for 2:4:6 T.N.T. gives a cal.val. of 509 cal./gm. Allowing for impurities in grade 1 T.N.T. it is best to take a figure of 500 cal./gm.

(g) Diethyl, Dibutyl and Diamyl phthalate. Ambler(23) obtained 7389 and 7705 cal./gm. for the heats of combustion of dibutyl and diamyl phthalate. Schmidt's figures were a little higher and the two figures were interchanged by mistake. Prosen and Gilmont(20) obtained 6419 and 7352 cal./gm. for samples of diethyl and dibutyl phthalate whose carbon contents were .9996 and .9985 times the calculated values for pure substances. Taking the mean of the two figures for dibutylphthalate the corresponding cal.vals. of the three substances are -1766, -2070 and -2190. Taylor and Hall obtained a cal.val. of -2025 cal./gm. for dibutylphthalate but this was obtained by firing a sample containing only 2% of this liquid. These large (negative) figures are not likely to be increased greatly by impurities in the materials and so since we are working to the nearest 5 cal./gm. we shall take -1765, -2070 and -2190 cal./gm. respectively for the cal.vals. of these liquids.

(h) Stabilisers and Graphite. Carbamite is the British name for diethyldiphenyl urea, sometimes called ethyl centralite or centralite I. Its heat of combustion is given by Schmidt(15) as 8528 cal./gm., 110 cal./gm. higher than Burlot's figure(17) and giving a negative heat of formation. Prosen and Gilmont obtained 8374 cal./gm., leading to a cal.val. of -2422 cal./gm. This is in fair agreement with Taylor and Hall's cal.val. figures of -2397 cal./gm. derived from heat of combustion and -2440 cal./gm. obtained from the cal.vals. of propellant mixtures. The last is the most reliable figure and we shall adopt it.

The cal.val. of methyl centralite was determined by Taylor and Hall as -2380 cal./gm. The value deduced from their heat of combustion measurement is -2303 cal./gm. but the directly determined cal.val. figure is the one that we should use. Schmidt's figure for the heat of combustion of akardite i.e. asymmetric diphenylurea, is 7700 cal./gm. giving a cal.val. of -2140 cal./gm. and a small negative heat of formation.

The composition of mineral jelly is not known accurately but the C:H ratio is a little higher than that calculated for a heavy aliphatic hydrocarbon. Some of the carbon-carbon bonds are therefore double. If 1% of the carbon bonds are double then the H content is 1% less than for a saturated aliphatic hydrocarbon and the negative cal.val. 80 cal./gm. smaller. The special mineral jelly used for M.D. cordite had a bromine number of 70 to 110 i.e. about .001 gm. moles of bromine reacted with 1 gm. of M.J. This implies that about 0.6% of the C-C bonds were double. For propellants containing carbamite ordinary mineral jelly of U.S. origin is used, for which the bromine number is given by Redwood(25) as about 10. We may therefore take present day M.J. to be practically pure paraffin containing 15 to 20 carbon atoms per molecule. If we take mineral jelly to be pure octadecane, $C_{18} H_{38}$, then Prosen and Rossini(26) give a heat of combustion at constant volume of 11256 cal./gm. leading to a cal.val. of -3305 cal./gm. For special M.J. used in M.D. we shall take a cal.val. of -3260 cal./gm. and a corresponding reduction in hydrogen content.

For diphenylamine the heat of combustion is given by Schmidt(15) as 9086 cal./gm. Figures of 9081, 9085 and 9049 cal./gm. are given by Burlot(17), Stohmann(27) and Lemoult(28). Kharasch's calculated figure(29) is 9118 cal./gm. No more modern figure has been found and so we shall take the mean, giving a cal.val. of -2660 cal./gm. For camphor Kharasch calculates a heat of combustion of 9283 and quotes an unpublished figure of 9274 cal./gm. by Swietoslawski. Taking 9276 cal./gm. we calculate a cal.val. of -2670 cal./gm. Schmidt(9)(15) gives heats of combustion for a number of other stabilisers which have been used in German propellants but which are of little immediate interest.

The cal.val. of pure graphite would be -3386 cal./gm. but the graphite used in propellants may contain up to 10% of impurities. We shall therefore take the figure of -3365 cal./gm. obtained directly by Taylor and Hall.

(i) <u>Solvents and Water.</u> The cal.val. of water is zero and the heat of wetting of N.C. in propellants is negligibly small. The heat of wetting of N.C. by acetone(30) is less than 1 cal./gm. when the acetone weight is less than 3% of the N.C. weight. Heats of wetting by ethyl ether and alcohol(31) are 2 cal./gm. for 2% and 3% solvent respectively. All these figures are negligible, for the amounts of solvent usually to be found in propellants.

The heat of combustion of acetone is 7282, 7351 or 7419 cal./gm. as calculated by Kharasch(29), measured by Berthelot and Delépine(32) or measured by Emery and Benedict(33). Taking the mean we get a cal.val. of -1930 cal./gm. with an uncertainty of 50 cal./gm. Fortunately acetone only occurs in small quantities in propellants.

Diethyl ether has a latent heat of vaporisation of 87 cal./gm. at 20°C. Thomsen(34) and Stohmann, Rodatz and Herzberg(35) measured the heat of combustion of the vapour and the latter also measured the heat of combustion of the liquid. Their figures corrected to the liquid state at constant volume, are 8811, 8818 and 8789 cal./gm. respectively. Taking the mean we get a cal.val. of -2100 cal./gm. For ethyl alcohol we have the very accurate heat of combustion, given by Rossini(36), of 7078 cal./gm. corrected to constant volume at 25°C. This gives a cal.val. of -1700 cal./gm. in round figures.

(j) <u>High explosives.</u> We use Schmidt's heat of combustion(29) of PETN which agrees closely with Burlot's figure. The A.R.E. Calorimetric section have found a cal.val. of 1360 cal./gm. for RDX in propellant mixtures and this is more reliable than figures of 1375 cal./gm. or 1370 cal./gm. calculated from Schmidt's or Burlot's heat of combustion. For tetryl both Schmidt and Stegeman(21) give a heat of combustion of 2925 cal./gm. agreeing closely with Burlot and leading to a cal.val. of 930 cal./gm. Stegeman gives heats of combustion of some thirty other explosives, mostly of only academic interest. A comprehensive collection of information on explosives is given by Blatt(40).

(k) <u>Liquid propellants.</u> The figures for methyl and ethyl nitrate, nitromethane, nitropropane and 85% hydrogen peroxide are taken from Wheeler et al.(37), those for nitric acid and liquid oxygen from Bichowsky and Rossini(38) and that for decane from the heat of combustion given by Rossini(39). The figure for liquid oxygen is the heat liberated in cooling oxygen gas from 300°K to 90°K and then liquifying it. Figures for hydrogen peroxide of any strength and for calcium permanganate are given in an unpublished report by Pike and Green.

The heats of formation have been given for constant pressure as well as constant volume conditions, for convenience in rocket calculations. The difference consists in adding

$$\tfrac{1}{2}\,RT\,\{(H) + (N) + (O)\}$$
$$= 298\,\{(H) + (N) + (O)\}\ \text{cal./gm.}$$

Finally the heat of formation of diamond is given for use in correcting heats of formation given by Bichowsky and Rossini(38).

2. Thermochemical data for the products of explosion.

(a) Heats of formation. The heats of formation of CO_2, CO, H_2O and CH_4 are taken from Wagman et al.(6), that of OH is derived from Dwyer's data(41), that of NO from Bichowsky and Rossini(39) and that of NH_3 from Gillespie and Beattie(42). Heats of dissociation into atoms are given by Herzberg(43). Figures for both 0°K and 300°K are given in Table 2.

(b) Free energies and equilibrium constants. The free energies of CO, H_2, N_2, O_2 and graphite have been interpolated from Wagman's data. Those of OH(44), NO(45), H(46), N(47) and O(48) have been corrected to new values of the fundamental constants(49) using similar methods to those used by Wagman. For CO_2 and H_2O completely new calculations have been made by the present author using the spectroscopic data given by Dennison(50), and adding the correction for rotational stretching term given by Wilson(51). The actual expressions used for CO_2 was

$$\begin{aligned}\frac{H_0^\circ - F}{T} &= 16.0148 \log T + 3.7640 + \frac{.374}{T} + .2385\ T\ .\ 10^{-5}\\ &+ 1.98718\,\{\ln(Qv)_1 + \ln(Qv)_2 + \ln(Qv)_3\}\\ &+ 4.57565 \log(1 + r)\end{aligned} \tag{8}$$

where
$$(Qv)_1 = \sum_{n=0}^{2242} \exp\left\{-\frac{1936.1}{T}\left[n - .000223\,(n^2 + n)\right]\right\} \tag{9}$$

$$(Qv)_2 = \sum_{n=0}^{256} (n + 1) \exp\left\{-\frac{961.26}{T}\left[n - .001945\,(n^2 + n)\right]\right\} \tag{10}$$

and
$$(Qv)_3 = \sum_{n=0}^{94} \exp\left\{-\frac{3415.6}{T}\left[n - .005264\,(n^2 + n)\right]\right\} \tag{11}$$

the upper limits for n being chosen such that the exponentials have their minimum value there. The actual values are of no importance in the present case but a finite upper limit must be chosen since the sums to infinity diverge. The last term 1 + r is composed of the cross terms in the vibrational levels, terms arising from the variation of moment of inertia with vibrational quantum numbers and also allows for the existence of rotations about the axis of symmetry when the moment of inertia about that axis is made non-zero by bending vibrations. The complete expression for r is

$$\begin{aligned}10^6 r = &- \frac{1000}{T}\left(1003\,\overline{n_2^2} + 2005\,\overline{n_2}\right)\\ &+ \left(1483\,\overline{n_1} - 1150\,\overline{n_2} + 7850\,\overline{n_3}\right)\\ &+ \left(2\,\overline{n_1^2} + \overline{n_2^2} + 62\,\overline{n_3^2}\right)\\ &- \left(3\,\overline{n_1}\,\overline{n_2} - 23\,\overline{n_1}\,\overline{n_3} + 18\,\overline{n_2}\,\overline{n_3}\right)\\ &+ \frac{1000}{T}\left(-\,8199\,\overline{n_1}\,\overline{n_2} + 31502\,\overline{n_1}\,\overline{n_3} + 15823\,\overline{n_2}\,\overline{n_3}\right)\\ &+ \frac{10^6}{T^2}\left(34\,\overline{n_1^2}\,\overline{n_2^2} + 496\,\overline{n_1^2}\,\overline{n_3^2} + 125\,\overline{n_2^2}\,\overline{n_3^2}\right)\\ &+ \frac{10^6}{T^2}\left(258\,\overline{n_1^2}\,\overline{n_2}\,\overline{n_3} + 130\,\overline{n_1}\,\overline{n_2^2}\,\overline{n_3} - 498\,\overline{n_1}\,\overline{n_2}\,\overline{n_3^2}\right)\end{aligned} \tag{12}$$

where

$$\overline{n_2^2}\ .\ (Qv)_2 = \sum_{n=0}^{256} n^2(n + 1) \exp\left\{-\frac{961.26}{T}\left[n - .001945\,(n^2 + n)\right]\right\} \tag{13}$$

and the other terms can be obtained in a similar manner. To calculate the sums of these series the $(n^2 + n)$ terms in the exponentials were expanded in series form, so giving an infinite series of sums of the form

$$\sum_{n=0}^{N} p(n)\, z^{n}$$

where $z = \exp\{-961.26/T\}$ etc. The error in taking N to be infinite was negligible and so each sum could be written down as a polynomial in z divided by a power of $(1 - z)$. The work was made much easier by the discovery of recurrence formulae for successive polynomials.

The corresponding expression for H_2O is

$$\begin{aligned}\frac{H_0^\circ - F^\circ}{T} = & - 8.1603 + 18.30268 \log T + \frac{4.170}{T} + 2.33\, T \,.\, 10^{-5} \\ & + 1.98718 \{\ln(Qv)_1 + \ln(Qv)_2 + \ln(Qv)_3\} \\ & + 4.57565 \log (1 + r)\end{aligned} \tag{14}$$

where

$$(Qv)_1 = \sum_{n=0}^{41} \exp\left\{-\frac{2350.46}{T}\left[n - .01193\,(n^2 + n)\right]\right\} \tag{15}$$

$$(Qv)_2 = \sum_{n=0}^{43} \exp\left\{-\frac{5376.7}{T}\left[n - .01141\,(n^2 + n)\right]\right\} \tag{16}$$

and

$$(Qv)_3 = \sum_{n=0}^{40} \exp\left\{-\frac{5535.5}{T}\left[n - .01241\,(n^2 + n)\right]\right\} \tag{17}$$

and

$$\begin{aligned}10^5 r = & \frac{81}{T}\left(1000 + 72\,\overline{n_1} - 126\,\overline{n_2} - 85\,\overline{n_3}\right) \\ & - \left(5019\,\overline{n_1} - 3101\,\overline{n_2} - 3343\,\overline{n_3}\right) \\ & - \left(133\,\overline{n_1^2} - 112\,\overline{n_2^2} - 104\,\overline{n_3^2}\right) \\ & - \left(49\,\overline{n_1}\,\overline{n_2} - 67\,\overline{n_1}\,\overline{n_3} - 34\,\overline{n_2}\,\overline{n_3}\right)\end{aligned} \tag{18}$$

These expressions are somewhat simpler than for CO_2 but the shortness of the Q series made it necessary to sum $(Qv)_1$ term by term for $T > 4000$ °K.

For CH_4 and NH_3 new calculations were made using the moments of inertia and vibrational frequencies given by Dennison in a rigid rotator, simple harmonic oscillator approximation but with Wilson's correction terms for rotational stretching added.

For perfect gases the formal relation for thermodynamic equilibrium between one group of gases and a second group into which the first can transform by chemical reaction is as follows:- Suppose the reaction to be

$$lA + mB + nC + \ldots \rightleftharpoons pX + qY + rZ +$$

where l,m,n, p,q,r etc. are the number of moles of each type A,B,C, X,Y,Z etc. being lost or gained in the reaction. Let the partial pressure of each type in equilibrium be P(A) etc., then the ratio of the products

$$\frac{\{P(X)\}^{p} \cdot \{P(Y)\}^{q} \cdot \{P(Z)\}^{r} \cdots}{\{P(A)\}^{l} \cdot \{P(B)\}^{m} \cdot \{P(C)\}^{n} \cdot} = K \tag{19}$$

where the equilibrium constant K is calculated from the relation

$$\begin{aligned}RT \ln K = & \{l\, F^\circ(A) + m\, F^\circ(B) + n\, F^\circ(C) + \ldots\} \\ & - \{p\, F^\circ(X) + q\, F^\circ(Y) + r\, F^\circ(Z) + \ldots\}\end{aligned} \tag{20}$$

where the free energy $F^\circ(A)$ etc. is calculated for one mole of each substance at temperature T but at unit pressure. Since the total free energy of one mole of

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any substance contains an additive term of R times the natural logarithm of its partial pressure we see that our equations are derived directly from the fact that for any system in reversible equilibrium the total free energy is at a minimum. In the tables we have taken unit pressure to be one atmosphere and for convenience we have tabulated $(H_0^\circ - F^\circ)/T$, where $(H_0^\circ - F^\circ)$ is the fall in free energy of one mole of the substance when its temperature is raised from 0°K to T at constant pressure and without change of state. If we assume that in the reaction we cool the initial substances to 0°K, carry out the reaction there and then raise the temperature of the products back to T then we can use the fact that at 0°K

$$-\Delta F_0^\circ = -\Delta H_0^\circ = \text{heat of reaction.}$$

We can therefore calculate the free energy change at 0°K from the heats of formation at that temperature given in table 2. These are calculated from heats of formation at room temperatures and specific heats over the range down to 0°K.

As an example consider

$$\tfrac{1}{2}H_2 \rightleftharpoons H$$

for which $$-\Delta H_0^\circ = 51620 \text{ cal./mole.} \quad \text{Writing}$$

$$K_1 = p(H)/\sqrt{\{p(H_2)\}}$$

then $$R \ln K_1 = -\frac{51620}{T} - \frac{1}{2}\left\{\frac{H_0^\circ - F^\circ}{T}\right\}_{H_2} + \left\{\frac{H_0^\circ - F^\circ}{T}\right\}_{H}$$

(c) Heat contents, entropies and specific heats. These were derived from the same sources as were the free energies, the data for OH and NO being corrected in a corresponding manner. For H, N and O it is sufficiently accurate to take the specific heat to be that of an ideal monatomic gas namely $C_v = 3R/2$, since these gases only occur in very small amounts. Data for CH_4 and NH_3 were calculated from Dennison's constants as before. The calculations for CO_2 and H_2O were based on expressions derived from those for the free energy by use of the formulae

$$\frac{H^\circ - H_0^\circ}{T} = T\frac{d}{dT}\left\{\frac{H_0^\circ - F^\circ}{T}\right\} \tag{21}$$

and $$C_p^\circ = C_v^\circ + R = dH^\circ/dT \tag{22}$$

where the superscript means ideal gas conditions i.e. at low pressures. The general term of each series for Qv was differentiated and in differentiating 1 + r use was made of the fact that the differential coefficient of n^{κ} can be expressed in terms of $n^{\kappa+1}$ etc. The resultant expressions are too lengthy to reproduce here.

The entropy at one atmosphere pressure was calculated in each case from the relation

$$F = H - TS$$

i.e. $$S^\circ = \frac{H^\circ - H_0^\circ}{T} + \frac{H_0^\circ - F^\circ}{T} \tag{23}$$

The enthalpy is not reproduced but H/T can be obtained if required by subtracting entries in the free energy table from corresponding entries in the entropy table. It was considered more useful to tabulate the mean specific heat at constant volume

$$\overline{C_v} = \frac{H_T^\circ - H_{300}^\circ}{T - 300} - R \tag{24}$$

since nearly all thermochemical calculations can be started from 300°K.

The tables have been entered at 100° intervals so that linear interpolation is sufficient in all cases except perhaps at temperatures below 2000°K. The logarithms of all the equilibrium constants except K_0 have been tabulated since these logarithms have almost constant first differences. Linear interpolation may lead to an error of a unit or two in the third decimal place for K_0 but the resultant error in the calculated temperature will amount to much less than 1°.

3. Calculation of the uncooled temperature of explosion, or adiabatic flame temperature.

We consider all solid propellants, including colloidal ones, to be simple mixtures i.e. neglect any heat of mixing there may be. Liquid propellants are usually not mixed before firing but if some components are so mixed e.g. hydrogen peroxide or nitric acid diluted with water the heat evolved in mixing is usually known and must be added to the heat of formation. We must be given, or we must estimate, the fraction by weight of each ingredient in the propellant. Multiplying each fraction by the heat of formation of unit mass of that ingredient and adding we get the heat of formation of unit mass of separated ingredients, to which must be added the heat of mixing, if any, to obtain the heat of formation of unit mass of propellant. By similar operations on the other columns of table 1 we can obtain the number of gram atoms of C, H, N and O in the propellant mixture.

For colloidal propellants and monopropellants composed of nitrated organic liquids such as nitromethane or ethyl nitrate, the products consist almost entirely of the five gases N_2, CO_2, CO, H_2O and H_2, the proportion of inflammable gases ($CO + H_2$) remaining being as high as 70 per cent in some cases. With bipropellant systems, the proportion of inflammable gas is often much lower and when hydrogen peroxide is used as a major component there may even be excess oxygen. Other bipropellant systems could be designed to produce gases containing excess oxygen, but for reasons of weight these are never used in practice unless the oxygen can be picked up from the atmosphere during burning.

Small amounts of inorganic materials are often included in colloidal propellants and large amounts in plastic propellants. At high temperatures these form oxides of metals, hydrides of halogens, etc. Sulphur forms H_2S plus a small proportion of SO.

At temperatures below 1,000°C., appreciable amounts of methane and ammonia will be formed in cases of oxygen deficit. In extreme cases solid carbon may separate out. At temperatures above 2,500°C. appreciable amounts of the dissociation products OH, H and NO will be formed and at still higher temperatures the other dissociation products O_2, O, N and C will begin to appear in that order.

In the very short time interval during which any element of propellant burns the change in gas pressure will be very small. The element therefore burns under constant pressure and makes room for itself by doing work on the gases previously formed. For explosion under constant pressure conditions the method of calculation of the temperature of such an element is as follows. We make a rough estimate of what that temperature will be and then calculate the composition of the gases in thermodynamic equilibrium at the estimated temperature. We then assume that the propellant decomposes completely into its final gaseous products at constant pressure and constant temperature, the heat evolved by the chemical reactions being stored in a reservoir. This heat is then taken out of the reservoir and used to heat the gaseous products at constant pressure up to the final temperature T_c. Symbolically:-

$$-\Delta H_R\,(T = T_0,\ P \text{ const.}) = \int_{T_0}^{T_c} C_p\,(\text{products})\,dT \qquad (25)$$

where C_p is the specific heat of the gaseous products at constant pressure.

Under constant volume conditions each element as it is produced does work not on the external world but on the other elements of gas produced previously, which will be compressed more or less adiabatically. The first element to be produced will suffer quite a high subsequent compression and so may be expected to reach a very high temperature while the last element to be formed will remain at temperature T_c. Convection currents or turbulent mixing will however rapidly reduce these temperature differences and the gas will take up a temperature T_1 given by the fact that the whole of the heat of reaction, at constant volume, is transferred to internal energy of the gas molecules, i.e.

$$-\Delta E_R\,(T = T_0,\ V \text{ const.}) = \int_{T_0}^{T_1} C_v\,(\text{products})\,dT$$

Since the heat of reaction at constant volume usually differs by only a few percent at most from that at constant pressure we have roughly, assuming T_0/T_c small

$$T_1 \approx \gamma T_0$$

where γ is a mean value of the ratio of specific heats over the temperature range up to T_0 and is of order 1.2 to 1.3.

All practical methods of calculation of the gas composition proceed by a series of successive approximations. There are four cases, each requiring different treatment. The first three are for calculations at temperatures below 2,700°C. or so and assume that the amounts of dissociation products are relatively small. The fourth method (d) makes no such assumption, but the total pressure cannot be predetermined. The first three cases are those of (a) oxygen deficit, (b) oxygen excess, and (c) oxygen balance.

Case (a) - oxygen deficit.

We start with 1 gram of propellant containing (C), (H), (N) and (O) gram atoms of each kind, the heat of formation of the solid propellant being h, and we wish to calculate the products formed at temperature T_0 under a total pressure P_0. If there are any inorganic elements present we estimate the products they form first and subtract the necessary amounts from our gram atoms of elements. We then assume that the remainder form only N_2, CO, CO_2, H_2O and H_2. Expressing quantities in gram moles we have

$$\left.\begin{aligned}(N_2) &= \tfrac{1}{2}(N)\\ (CO) &= (C) - (CO_2)\\ (H_2O) &= (O) - (C) - (CO_2)\\ (H_2) &= \tfrac{1}{2}(H) - (O) + (C) + (CO_2)\end{aligned}\right\} \qquad (26)$$

these equations expressing the equality of the number of atoms of each type before and after the reaction. The water gas equilibrium gives us:

$$(CO) \times (H_2O) = K_0(CO_2) \times (H_2)$$

this equilibrium being independent of pressure. Eliminating (CO), (H_2O) and (H_2) by means of the previous equations, we are left with a quadratic equation for (CO_2), the solution of which is:-

$$(CO_2) = -b \pm \sqrt{b^2 + (C)\{(O) - (C)\}/\{K_0 - 1\}} \qquad (27)$$

where $$b = [(O) + K_0\{\tfrac{1}{2}(H) - (O) + (C)\}]/2(K_0 - 1) \qquad (28)$$

Only one of the two solutions for (CO_2) gives positive quantities for all the products. We can now write down the number of gram moles of each of the major gases, and, by proportion, their partial pressures.

The next stage is to calculate the partial pressures of the dissociation products. The equilibrium equations should preferably express each dissociation product in terms of the major products only. For example, we should use the equation:-

$$p(O) = K_5 p(H_2O)/p(H_2)$$

rather than

$$p(O) = (K_5/\sqrt{K_6})\sqrt{p(O_2)}$$

since $p(O_2)$ will not be known very precisely. The partial pressures of the dissociation products can now be converted into gram moles using the same factor of proportionality as for the major gases. These dissociation products are formed by reducing the amounts of the major gases and so we must subtract the corresponding amounts from the (N), (C), (H) and (O) available for the major gases. We then repeat the calculation of the amounts of these major gases.

Very often we can guess these amounts without solving the quadratic again; a useful rule is to keep the amount of the smallest constituent, usually H_2, the same as before. If the amounts of the major products have been appreciably altered, it may be necessary to recalculate the dissociation products again.

Having calculated the gas composition at the given total pressure, and estimated temperature, we can calculate the heat of reaction at room temperature. This is simply the sum of the heats of formation of the gaseous products minus the heat of formation of the initial propellant. The heat required to raise the gaseous products from room temperature to temperature T_c can be calculated using tables of mean specific heats of the gaseous products over this temperature range. If this is less than the heat available, i.e. the heat of reaction, the true value of T_c will be somewhat higher, and vice versa. We can make a slight over-estimate of the amount we have to raise T_c by dividing the excess heat available by the specific heat at temperatures near T_c. If the original estimate of T_c was in error by 100° or more it may be necessary to repeat the whole calculation for a second estimated value of T_c and then determine the true temperature by interpolation.

Case (b) - oxygen excess.

This case is a little easier than (a) because we have no quadratic equation to solve. The major products are:-

$$\left.\begin{aligned}(N_2) &= \tfrac{1}{2}(N)\\ (CO_2) &= (C)\end{aligned}\right\}$$

$$\left.\begin{aligned}(H_2O) &= \tfrac{1}{2}(H)\\ \text{and}\quad (O_2) &= \tfrac{1}{2}(O) - (C) - \tfrac{1}{4}(H)\end{aligned}\right\} \qquad (29)$$

The minor products are CO, H_2, OH, NO, H, O, N and C, usually in that order of magnitude. The equilibrium equations should express the partial pressures of these eight dissociation products in terms of the four major gases. Calculation then proceeds as in case (a).

Case (c) - oxygen balance.

In this case we have only three major products and the calculation of the minor products is more difficult. The best procedure is to calculate the biggest minor product first, namely CO. We have

$$(H_2) \doteq \frac{1}{K_0}\frac{(H_2O)}{(CO_2)}(CO) \approx \frac{(H)}{2K_0(C)}(CO) \qquad (30)$$

and

$$(O_2) = \tfrac{1}{2}\{(CO) + (H_2)\} \qquad (31)$$

if we assume that CO and H_2 are the only minor products. We also have

$$p(O_2) = K_0^2K_6\{(CO_2)/(CO)\}^2 \qquad (32)$$

and from these three equations we get, since

$$(CO_2) = P_c(C)/\{(C) + \tfrac{1}{2}(H) + \tfrac{1}{2}(N)\}, \qquad (33)$$

$$(CO)^3 = 4K_0^3K_6(C)^3\{(C) + \tfrac{1}{2}(H) + \tfrac{1}{2}(N)\}/\{2K_0(C) + (H)\}\,P_c \qquad (34)$$

where P_c is the total pressure. This gives us a first estimate of (CO), using which we can calculate (H_2) from the exact equation and then (O_2). We can then get a better estimate of (CO) by inverting equation (32) and so can repeat the cycle.

Case (d) - large amounts of dissociation.

In such cases the separation into major and minor components and calculation by successive approximations may become very tedious and an entirely different method of approach has been devised by Lutz(52). This method depends on the fact that, with the exception of NO, the partial pressures of all the components can be expressed in terms of two parameters. One of these parameters, namely the ratio

$$x = (CO_2)/\{(CO) + (CO_2)\} \tag{35}$$

can be determined from the initial atomic proportions by use of a universal chart. The other parameter is the partial pressure of H_2O. A value must be given to this parameter and the calculation carried right through, the total pressures being obtained as the sum of the partial pressures. If this total pressure is not the value required, the calculation must be repeated with a different initial value of $p(H_2O)$. The method is therefore one of trial and error. Having calculated the gas composition for the required temperature and pressure, the rest of the calculation follows normal lines.

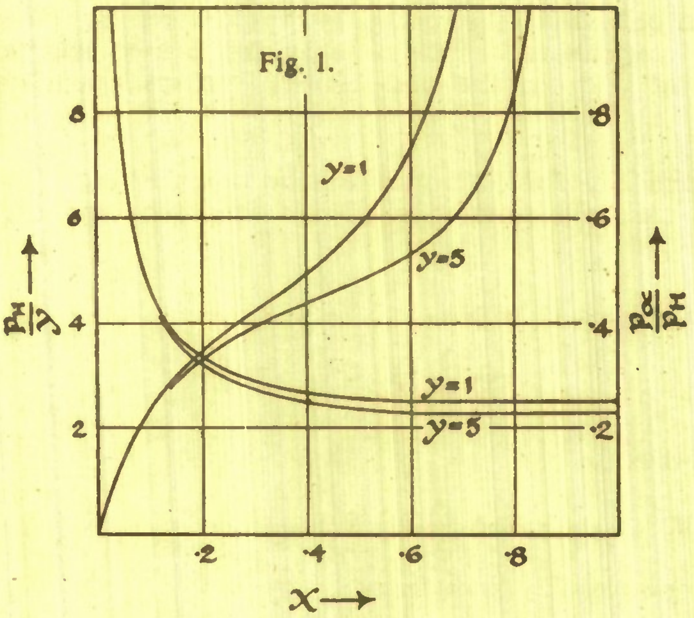
Fig. 1.

An outline of Lutz's method is as follows:-

We write:-

$$a = x/(1 - x) = p(CO_2)/p(CO) \tag{36}$$

$$y = p(H_2O) \tag{37}$$

$$p_C = p(CO_2) + p(CO) \tag{38}$$

$$\begin{aligned} p_H &= 2p(H_2O) + 2p(H_2) + p(OH) + p(H) \\ &= 2y + \frac{2y}{K_0 a} + K_2\sqrt{K_0 a y} + K_1\sqrt{\frac{y}{K_0 a}} \end{aligned} \tag{39}$$

and

$$\begin{aligned} p_o &= 2p(CO_2) + p(CO) + \cancel{p(H_2O)} + \cancel{p(OH)} + \\ &\quad + \cancel{2p(O_2)} + \cancel{p(O)} + \cancel{p(NO)} \\ &= (1 + x)\, p_C + \cancel{\{y + K_2\sqrt{K_0 a y} + 2K_0^2 K_6 a^2} \\ &\quad \cancel{+ K_5 K_0 a\}} + \cancel{p(NO)} \\ &= (1 + x)\, p_C + p_\alpha + p(NO) \text{ say} \end{aligned} \tag{40}$$

If we divide this last equation through by p_H we have

$$\frac{p_o - p_C}{p_H} - x\frac{p_C}{p_H} = \frac{p_\alpha}{p_H} + \boxed{\frac{p(NO)}{p_H}}\ \text{negligible} \tag{41}$$

Since p_o, p_C, etc., are proportional to (O), (C), etc., the left-hand side is a known linear function of x for any given composition. If we omit the small correction term p(NO) then the right-hand side is a function of x (or a) only for a given value of y for a given temperature, since the Ks are functions of T only. For any one temperature, therefore, a chart can be prepared on which p_α/p_H is graphed as a function of x for a series of values of y. The curves do not differ greatly with variation in y.

For any given mixture the straight line given by the left-hand side of equation (41) can be drawn on the chart and where this intersects the p_α/p_H curve gives the correct values of x and p_α/p_H for a given y. Given the values of x and y, we can calculate the partial pressures of all the hydrogen compounds and so p_H by summation. We can then calculate p_C and p_N by proportion and so the partial pressures of the remaining components. The calculation can be shortened slightly if we plot a set of curves of p_H/y on the same chart. These again are functions of x and y only.

We can correct approximately for NO formation by calculating $p(NO)/p_H$ and then subtracting this from the left hand side of our equation, so slightly lowering the line. We have

$$\{p(NO)/K_3K_6a\}^2 = p(N_2)$$

$$= \frac{(N)}{2(H)} p_H - \tfrac{1}{2} p(NO)$$

giving to a fair approximation

$$p(NO)/p_H = K_3K_6a \sqrt{\{(N)/2(H)p_H\}}$$

A second approximation is not usually necessary.

The method requires the preparation of a chart for each value of T, say every 100°, over the range of interest but these charts can be prepared once and for all.

Fig. 1 shows a simplified diagram for T = 3,000°K. It can be seen that the curves do not differ greatly for quite large changes in y, so that we do not have to guess the initial value of the partial pressure of H_2O very exactly. Of course, in practice curves would be drawn on the diagram for a considerable number of values of y. For temperatures below 2,500°K the curves coincide for all practical values of y and x and the method then degenerates into a graphical method of solving the quadratic equation (27) for (CO_2).

Having calculated the gas composition at the given total pressure or volume and the assumed temperature we use the table of mean specific heats to calculate the heat required to raise that gas mixture to that temperature from 300°K. This should equal the heat of reaction available for the purpose, namely the heat of formation of the gaseous products which can be calculated from table 2, less the heat of formation of the initial propellant, the whole calculation being carried out for constant pressure or constant volume as the case may be. If equality is not attained the whole calculation must be repeated for another assumed temperature T_0 or T_1. For an experienced operator two such calculations are usually sufficient.

Finally mention should be made of a very simple approximate method of calculation developed by Hirschfelder and Sherman(53). This can only be used as it stands for mixtures deficient in oxygen and for very small amounts of dissociation, so that it is mainly of value for gun propellants. For values of T_1 between 2000 and 3000°K the three equations to be used are

$$n = \sum_i x_i n_i \qquad (42)$$

$$C_v = \sum_i x_i C_{vi} \qquad (43)$$

and

$$T_1 = 2500 + (\sum_i x_i E_i)/C_v \ {}^\circ K \qquad (44)$$

where x_i is the fraction by weight of the i th constituent of the propellant and n_i, C_{vi} and E_i are tabulated for all the usual propellant ingredients. For temperatures over 3,000°K dissociation reduces T_1 appreciably and a more elaborate formula is given for T_1 in such cases. Strictly speaking their table should be modified slightly to bring it into line with the more accurate thermochemical data now available but the approximate nature of their method renders this unnecessary.

4. Corrections for gas imperfections.

Under rocket conditions i.e. temperatures greater than 1,000°C and pressures less than 100 atmospheres, we may treat the gaseous products as a mixture of perfect gases. For gun conditions however the pressures are of such a magnitude that fairly simple corrections are both necessary and sufficient. Gun calculations invariably come under case (a).

These pressure corrections are treated fully by Corner(3) but for convenience a short abstract of his paper is given here. In the first place the equation of state of such a gas mixture is represented with sufficient accuracy by

$$PV = nRT\,(1 + B/V + nC/V^2) \tag{45}$$

where B and C are additive functions of the constituents of the gas mixture, e.g.

$$B = (CO_2)\cdot B(CO_2) + (CO)\cdot B(CO) + \ldots \tag{46}$$

and similarly for C. The water gas equilibrium constant is multiplied by the factor

$$\exp\,(-\,n\,\Delta B/V - n^2\,\Delta C/2V^2)$$

where

$$\Delta B = B(CO) + B(H_2O) - B(CO_2) - B(H_2) \tag{47}$$

with a similar expression for ΔC. The only other equilibrium constants that need correcting are K_2 and K_3 and it is sufficient to multiply each by $\exp\,(-\,20\,n/V)$.

The internal energy at some temperature T can be written

$$E - E_{300} = \Sigma(CO_2)\,E_0(CO_2) + \frac{n}{V}\,\Sigma(CO_2)\cdot E_1(CO_2) + \left\{\frac{n}{V}\right\}^2 \Sigma(CO_2)\,E_2(CO_2) \tag{48}$$

where the summation signs indicate sums over all the constituents of the gaseous mixture. The first term is the energy of the gases assumed perfect relative to the same perfect gases at 300°K, and the correction terms E_1 and E_2 for the various gases are given by Corner. The nett correction to E is always negative. It should be noted that no correction is to be applied to the heat of reaction, which has been corrected to perfect gas conditions in preparing our tables of heats of formation.

For imperfect gases it is best to work in terms of partial densities, not partial pressures, the equilibrium equations are then used in the form

$$\frac{(CO)\cdot(H_2O)}{(CO_2)\cdot(H_2)} = K_0\,\exp\left\{-\frac{n\Delta B}{V} - \frac{n^2\Delta C}{2V^2}\right\} \tag{49}$$

$$(H) = K_1\,\sqrt{\{(H_2)\,V/82.06\,T\}} \tag{50}$$

$$(OH) = K_2\,(H_2O)\,\sqrt{\{V/82.06\,T(H_2)\}}\,\exp\,\{-\,20\,n/V\} \tag{51}$$

$$(NO) = \frac{K_3\,(H_2O)}{(H_2)}\bigg/\left\{\frac{(N_2)\cdot V}{82.06\,T}\right\}\exp\left\{-\frac{20\,n}{V}\right\} \tag{52}$$

$$(N) = K_4\,\sqrt{\{(N_2)\,V/82.06\,T\}} \tag{53}$$

$$(O) = K_5\,\frac{(H_2O)}{(H_2)}\,\frac{V}{82.06\,T} \tag{54}$$

and

$$(O_2) = K_6\,\frac{(H_2O)^2}{(H_2)^2}\,\frac{V}{82.06\,T} \tag{55}$$

where the bracketed quantities are moles per gram of mixture, V is the given volume of one gram of mixture and n the total number of moles of gas in one gram of mixture For use in these equations it is usually sufficiently accurate to calculate n assuming no dissociation, i.e. to put

$$n = (C) + \tfrac{1}{2}\,(H) + \tfrac{1}{2}\,(N) \tag{56}$$

where in this equation the quantities on the right hand side are the total number of gram atoms of C, H and N per gram of propellant.

Having completed the calculation of T_1 we can compute B and C in the equation of state and so the pressure P. But in internal ballistic calculations for guns it is far more convenient to use an equation of state of the form

$$P(V - \eta) = nRT \tag{57}$$

where the co-volume η is taken to be constant. If we choose a suitable value for V near the minimum value that occurs in the gun then we can calculate a value of η that gives the correct pressure at that gas density and very nearly the correct value at all densities since at low pressures the effect of corrections for gas imperfection diminish. It is customary to take V = 5 c.c./gm. and so we have

$$\eta = \frac{25B + 5nC}{25 + 5B + nC} \tag{58}$$

Since the C term is relatively small and $B \sim 1$, we find η to be of the order of 80% of B.

Corner also gives a rough formula for estimating η, namely

$$\eta = 1.18 + 6.9\,(C) - 11.5\,(O) \tag{59}$$

where the quantities on the right hand side are gram atoms per gram of propellant.

For calculating the effective value γ of the ratio of specific heats for use in gun calculations we must allow for heat liberated by chemical reactions as the gases cool, assuming thermodynamic equilibrium to be maintained as is almost certainly the case at the high temperatures and pressures obtaining in the gun. For this purpose we assume that when the base of the projectile reaches the muzzle T has fallen to 0.6 times its uncooled value, and V has risen to 10 c.c./gm. We then calculate the gas composition in equilibrium under those conditions, an easy calculation since there will be no dissociation. The difference between the heat of reaction available and the heat content of the gases, relative to ideal conditions at 300°K, gives the energy lost to external work. If we call this energy loss ΔE then we have

$$\gamma = 1 + \frac{0.4\,nRT}{\Delta E} \tag{60}$$

where γ is the effective mean value that we require.

5. The use of entropy tables in calculating rocket thrusts.

In a gun we only get adiabatic conditions after the charge is all burnt and it is sufficient to use the mean value of γ as defined above, but as a general rule the use of a constant γ is not suitable for calculating the thrust obtainable from a rocket.

The total thrust given by a rocket motor is the resultant force of the gas pressure acting over all surfaces of the motor. If P_e, the pressure at the exit of the nozzle, equals P_α, the atmospheric pressure, then the atmosphere produces no resultant thrust on the motor. Otherwise there is an additional thrust equal to $(P_e - P_\alpha)$ multiplied by the nozzle exit area. The main component of thrust is equal to the rate of generation of momentum i.e. the product of the gas exit velocity multiplied by the mass discharged per second.

The calculation of the pressure-temperature relation in the adiabatic expansion through the nozzle is more difficult if there are appreciable quantities of dissociated gases in the chamber since these may recombine as their temperature falls while they go through the nozzle. There is some doubt about the speed of this recombination, but at the very high temperatures at which an appreciable amount of dissociation occurs chemical reactions are extremely fast and it seems reasonable to suppose that chemical equilibrium is maintained at least as far as the nozzle. This means that most of the recombination will take place and so we shall not be far wrong if we assume it to be complete.

In calculating the pressure-temperature relation there is some advantage to be gained if we make use of the condition of constant entropy. We must first calculate the gas composition at the temperature T_c in the chamber and at a total pressure P_c. If $S^o(CO_2)$ is the entropy of one mole of CO_2 at the given temperature and a partial pressure of one atmosphere then the entropy per gram of our gas mixture at temperature T and pressure P is

$$S = \Sigma\ (CO_2)\ S^o(CO_2) - R\ \Sigma\ (CO_2)\ P(CO_2) \qquad (61)$$

where $P(CO_2)$ is the partial pressure of CO_2. Taking the gases to be perfect we have

$$P(CO_2) = P\ .\ (CO_2)/n$$

and so

$$S = S^o - Rn \ln P - Rn\ \Sigma \frac{(CO_2)}{n} \ln \frac{(CO_2)}{n} \qquad (62)$$

where we have written S^o for the first sum.

Usually the final pressure P_e is stipulated and so we must calculate the gas composition and entropy for at least two temperatures at that pressure. The correct temperature can then be interpolated.

If no changes in chemical composition occur then the last term in equation (62) remains constant and, since we are only interested in differences of entropy, it need not be calculated. For an adiabatic expansion we then have $\delta S = 0$

i.e. $$Rn\ \delta\ (\log P) = \delta\ S^o = \frac{n.C_p}{T}\ \delta\ T \qquad (63)$$

where $$n\ Cp = \Sigma\ (CO_2)\ Cp(CO_2) \qquad (64)$$

We can calculate the increase in kinetic energy of the gases from the relation:-

$$\tfrac{1}{2}\ \delta\ (v^2) = -\ nC_p\ \delta T \qquad (65)$$

or $$\tfrac{1}{2}\ \delta\ (v^2) = RTn\ \delta\ (\ln P) \qquad (66)$$

If chemical changes occur during the expansion then for no change in total entropy we have

$$\tfrac{1}{2}\ \delta\ (v^2) = -\ n\ \delta\ H \qquad (67)$$

where we have generalised $-\ \delta\ H$ to include not only $-\ C_p\ \delta T$, the purely thermal energy liberated, but also the heat liberated by the chemical reactions occurring during the small temperature drop. Some writers use a generalised H which satisfies equation (67) and which is defined by the relation:-

$$nH = \Sigma\ (CO_2)\ H'(CO_2) \qquad (68)$$

where $$H'(CO_2) = \int_0^T C_p(CO_2)dT - (\text{H.F. of } CO_2 \text{ at } 0°K) \qquad (69)$$

H' will then have normal values for elementary gases such as H_2 and N_2 but large negative values for such gases as CO_2, CO and H_2O. With these generalised enthalpies equation (67) will be true whether chemical changes take place or not.

For any given gas mixture, diagrams connecting total entropy, generalised enthalpy, pressure and temperature can be constructed in precisely the same way as for steam. Such diagrams are, however, only accurate for that particular mixture and so are rarely worth constructing. For a series of mixtures a series of diagrams would have to be constructed but if the whole series had equal values of some parameter, such as the molar fraction of triatomic gases in the mixture, then the diagrams would be nearly the same and for rough calculations a general diagram could be used. A good deal of calculation on these lines has been carried out by German scientists.

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Equation (66) is always true and this equation does not contain C_p. Hence for a small pressure drop the gain in kinetic energy of the gases is independent of whether or no the heat liberated is increased by chemical reactions, provided we start from the same initial conditions. Since most of the chemical reaction, if it does occur, will occur during the first 200° fall in temperature its effect on the thrust will be quite small. Unless, therefore, the dissociation is sufficient to lower the chamber temperature by more than 100° or so the thrust can be calculated with sufficient accuracy for most purposes by a simplified calculation assuming that no chemical reactions take place in the nozzle.

Once we have calculated the temperature and composition of the gases under a given pressure P_c in the combustion chamber, by one of the methods outlined in section 3, the simplified calculation for the adiabatic expansion is very easy. In an adiabatic expansion the total entropy S remains constant but, since we are assuming the gas composition to remain constant, the third term on the right-hand side of equation (62), which is in fact the entropy of mixing of the gases, remains constant and so need not be calculated. Under these conditions in an adiabatic expansion $S^0 - Rn \log P$ remains constant. S^0 is a function of temperature only and can be readily calculated from tables for a given gas mixture. The procedure is to calculate S^0 at the combustion chamber temperature T_c and then at some lower temperature T_2. Since S remains constant we have:-

$$S^0(T_c) - S^0(T_2) = Rn\,(\ln P_c - \ln P_2) \qquad (70)$$

from which we can calculate the pressure P_2 of the gas corresponding to the temperature T_2. By choosing two or more values of T_2 and then interpolating we can calculate the value of T_e corresponding to the nozzle exit pressure P_e.

The kinetic energy of the gases issuing from the nozzle will equal the decrease in their enthalpy H, which is a function of temperature only, for a given gas mixture. $H(T_c)$ has been calculated already in evaluating T_c. We then calculate $H(T_e)$ and we have:-

$$\tfrac{1}{2}\, v_e^2 = H(T_c) - H(T_e) \qquad (71)$$

The specific impulse is the gas momentum produced per unit mass of propellant consumed and if the products are entirely gaseous this is simply v_e or v_e/g in practical units. The thrust on the motor is this quantity multiplied by the mass rate of consumption of propellant. We are, of course assuming expansion to atmospheric pressure in the nozzle. The specific impulse increases slowly with chamber pressure and strictly speaking should be corrected to some standard chamber pressure, say 20 atmospheres. Since in practice the range of chamber pressures used is not very wide this correction is usually omitted.

6. Numerical examples.

To illustrate the various methods of calculation we give two examples, one for a gun propellant with very little dissociation of the gaseous products and one for a highly dissociated rocket propellant.

(a) Calculation for S.C. in a constant volume of 5 c.c./gm.

S.C. may contain some .2% by weight of water and say .5% of inert material, such as chalk, iron oxide, silica etc. which occur as impurities in the nitrocellulose. Taking nominal proportions of the dry ingredients we get the following composition per gm.

NC	.48902 gms. of 12.3% N (actual)		
NG	.41417		
Carb.	.08982	Cal.val. (calculated)	954 cal./gm.
H_2O	.00200	H.F.	477 cal./gm.
Inert	.00499		

First of all using Hirschfelder's simple method we have, assuming a specific heat of .3 cal./gm. °K for the inert material which absorbs heat but contributes nothing to the pressure,

$n = .04233$ gm. moles/gm.

$C_v = .35013,\ \gamma = 1 + 1.987\, n/C_v = 1.240$

$T_1 = 2500 + 217.55/.35013 = 3121$ °K.

The temperature will be a little lower on account of dissociation, say 3100°K, which we shall use as our first estimate for the method of case (a). The atomic composition is

$(C) = .022107$ gm. atoms/gm.

$(H) = .029984$

$(N) = .010435 \qquad n \sim (C) + \frac{1}{2}(H) + \frac{1}{2}(N) = .042317$

$(O) = .034569$

[Check $.00499 + 12.010 \times .022107 + 1.008 \times .029984 +$ etc. $= .999996$ gms.]

$(CO) = .022107 - (CO_2)$

$(H_2O) = .012462 - (CO_2)$

$(H_2) = .002530 + (CO_2)$

and $\qquad K = 7.923 \exp\{.2674 + .0183\} = 10.543$

Hence $\qquad (CO_2) = -\ .003209 + \sqrt{.0000391655} = .003049$

Our calculated products are now

$(CO_2) = .003049$ gm. moles

$(H_2O) = .009413$ " " $\qquad$ [Check $(H_2O) \cdot (CO) = .00017939$

$(CO) = .019058$ " " $\qquad$ $K\,(H_2) \cdot (CO_2) = .00017934$]

$(H_2) = .005579$ " "

$(N_2) = .005218$ " "

Inert $= .00499$ gms.

and from these we calculate the following byproducts, using equations (50) to (52)

$(H) = .2121 \sqrt{\{.005579/(16.412 \times 3100)\}} = .000070$

$(OH) = .07695 \times .009413/1.1845 \sqrt{\{16.412 \times 3100 \times .005579\}}$

$= .000036$

and $\qquad (NO) = .008519 \times .009413 \sqrt{\{.005218\}}/1.1845 \times .005579 \sqrt{\{16.412 \times 3100\}}$

$= .000004$

the other byproducts being negligible. Subtracting these from the gm. atoms available for the main products we have

$(C) = .022107$ gm. atoms/gm.

$(H) = .029878$ " " " $\qquad n = (C) + \frac{1}{2}(H) + \frac{1}{2}(N) + .000110$

$(N) = .010431$ " " " $\qquad = .042372$

$(O) = .034529$ " " "

$(CO) = .022107 - (CO_2)$

$(H_2O) = .012422 - (CO_2)$

$(H_2) = .002517 + (CO_2)$

and $\qquad K = 7.923 \exp\{.2678 + .0183\} = 10.547$

We can now find the major products by solving the quadratic or by trial. The changes are so small as to render recalculation of the major products unnecessary and we have for the complete composition of 1 gm.

Subst.	Amount	H.F.	$\overline{C_v^o}$
(CO_2)	.003046 gm. moles.	94052 cal./mole.	11.562 cal./mole. °K
(H_2O)	.009376	57504	9.288 .. ..
(CO)	.019061	26711	6.312 .. ..
(H_2)	.005563	-	5.881 .. ..
(N_2)	.005216	-	6.245 .. ..
(H)	.000070	-51794	2.981 .. ..
(OH)	.000036	- 9903	5.988 .. ..
(NO)	.000004	-21600	6.445 .. ..
Inert	.00499 gm.	-	0.3 cal./gm. °K
	n = .042372 ,	H.F. = 1330.7 cal./gm. ,	$\overline{C_v^o}$ = .30979 cal./gm. °K

The nett heat available from the reaction is 1331 - 477 = 854 cal./gm., the reduction from the cal.val. being due to the water now being gaseous. The heat required to heat the products at constant volume but at very low pressure from 300°K to 3100°K is E_0 = .30979 × 2800 = 867 cal./gm. but to this must be added the negative terms due to gas imperfections as explained in section 4. Using Corner's tables we have

$$E_{3100} - E_{300} = 867 - .0084744 \times 428 + (.0084744)^2 \times 18404$$
$$= 867 - 3.6 + 1.3 = 865 \text{ cal./gm.}$$

This exceeds the heat available by 11 cal./gm. Using table 7 we find that the specific heat of the products at 3100°K is .356. The true value of T_1 will therefore be a little higher than 3100 - 11/.356 = 3069°K because the heat of reaction will be a little greater at that temperature. The main difference is that the byproducts are reduced by a factor of about 0.7 for a drop in temperature of 100°K and the heat absorbed in dissociation at 3100°K is 6.4 cal./gm. in the present case. A better estimate of T_1 is therefore 3100 - 10/.356 = 3072°K.

At that temperature we have by interpolation of table 4, K_1 = .1952, K_2 = .06931, K_3 = .007524 and since the changes in the major products will be small we have for the new values of the byproducts

$$(H) = .000070 \times .1952/.2121 = .000065 \text{ gm. moles.}$$

similarly (OH) = .000033, (N) = .000004 gm. moles.

Allowing for the increase in the major products of $\frac{1}{2}\{.000005 + .000003\}$ and a decrease in the minor products of twice that amount we have n = .042368 gm./moles/gm. Interpolating K_0 we have

$$K = 7.868 \exp\{.2678 + .0184\} = 10.475$$

and
$$(H_2O) = .012425 - (CO_2)$$
$$(CO) = .022107 - (CO_2)$$
$$(H_2) = .002518 + (CO_2)$$

We can find the major products by trial and the final composition at 3072°K is as follows.

Subst.	Amount	H.F.	$\overline{C_v^o}$
(CO_2)	.003056 gm. moles.	94052 cal./mole.	11.549 cal./mole °K
(H_2O)	.009369	57504	9.266 .. ..
(CO)	.019051	26711	6.306 .. ..
(H_2)	.005574	-	5.871 .. ..
(N_2)	.005216	-	6.238 .. ..
(H)	.000065	-51794	2.981 .. ..
(OH)	.000033	- 9903	5.979 .. ..
(NO)	.000004	-21600	6.439 .. ..
Inert	.00499 gm.	-	.3 cal./gm. °K
	n = .042368 ,	H.F. = 1331.3 cal./gm. ,	$\overline{C_v^o}$ = .30942 cal./gm. °K

Hence $E_{3072} - E^{\circ}_{300}$ = 855 cal./gm. since the pressure correction will be -2 cal./gm. as before. The heat available is 854 cal./gm. so the true temperature is 3070°K, the composition being unchanged from the above. The force constant is

$$\lambda = .5384\ n\ T_1 = 70.03 \text{ tons/sq.in./gm./c.c.}$$

or

$$= 1938 \text{ inch tons/lb.}$$

The corresponding figure calculated by the simple method is 1% higher.

To calculate γ we must calculate the gas composition at 0.6 × 3070 = 1842 °K and at a volume of 10 c.c./gm. There will be no byproducts and the water gas equilibrium constant is

$$K = 4.177 \exp \{.1413 + .0076\} = 4.848$$

The products are now

Subst.	Amount	H.F.	$\overline{C_v^\circ}$
(CO_2)	.004337 gm. moles.	94052 cal./mole.	10.688 cal./mole. °K
(H_2O)	.008125	57504	8.042 .. ..
(CO)	.017770	26711	5.916 .. ..
(H_2)	.006867	-	5.375 .. ..
(N_2)	.005218	-	5.833 .. ..
Inert	.00499 gm.	-	.25 cal./gm. °K

n = .042317 , H.F. = 1350 cal./gm. , $\overline{C_v^\circ}$ = .28542 cal./gm. °K

$$E_{1842} - E^{\circ}_{300} = 440.1 - 4.9 + .4 = 436 \text{ cal./gm.}$$

$$\text{Heat available} = 1350 - 477 = 873 \text{ cal./gm.}$$

Hence the nett loss of internal energy when the temperature falls from 3070 to 1842°K is 437 cal./gm., so over that range $\overline{C_v}$ = .3559, $\overline{n}$ = .042343 and so γ = 1.2364. This compares with 1.240 as calculated by the simple method.

The second and third virial coefficients in the equation of state calculated at 3070°K are

$$B = 1.1170 \text{ c.c./gm.}$$

$$n\,C = .2570 \text{ (c.c./gm.)}^2$$

Hence from equation (58) η = .947 c.c./gm. Allowing for the volume of the inert solids would increase this by about two units in the third decimal place, we may therefore round off this figure to .950 c.c./gm.

The value of η calculated for V = 10 c.c./gm., T = 1842°K is 1.002 c.c./gm. but since the co-volume is much less important here it is sufficient to take the constant value of .950 c.c./gm. The simple formula equation (59) suggested by Corner gives η = .935 c.c./gm. which is sufficiently accurate for most purposes.

(b) Calculation for a 1:3 mixture by weight of decane and liquid oxygen under a constant pressure of 50 atmospheres.

Decane has been chosen as a representative paraffin. The mixture gives values of T_c of the order of 3600°K and so large amounts of dissociation. We shall therefore start by using Lutz's graphical method. The atomic composition of this mixture is

(C) = .017572 gm. atoms/gm.
(H) = .038657 .. .. ..
(O) = .046875 .. .. ..

H.F. = 199 cal./gm. at C.P.

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We shall use Lutz's method(52) to find the gas composition at 3600°K. Since $p(H_2O)$ must be of order 20 atmospheres we see from his graph that x must lie between .4 and .5, but since his equilibrium constants differ from ours, particularly for OH, we shall draw our own curves of p_α/p_H for y = 20 and y = 16 atmos. and for values of x extending only from .36 to .50. Putting in our own equilibrium constants we have

$$p_\alpha\ (y = 20) = 20 + 4.808\ \sqrt{a} + 1.410\ \ a + 9.102\ a^2$$

$$p_\alpha\ (y = 16) = 16 + 4.300\ \sqrt{a} + 1.410\ \ a + 9.102\ a^2$$

$$p_H\ (y = 20) = 40 + 4.808\ \sqrt{a} + 1.112/\sqrt{a} + 4.575/a$$

$$p_H\ (y = 16) = 32 + 4.300\ \sqrt{a} + .944/\sqrt{a} + 4.300/a$$

where $a = x/(1 - x)$. The intersecting line is

$$.75803 - .45456\ x$$

and the points of intersection give

$$y = 20, \quad x = .4135, \quad p_H = 51.85, \quad a = .7050$$

$$y = 16, \quad x = .3977, \quad p_H = 42.26, \quad a = .6603$$

From our equilibrium constants we can now calculate two trial solutions, the quantities in gm. moles being calculated from the partial pressures

Gas	p atmos.	gm. moles/gm.	p atmos.	gm. moles/gm.
H_2O	20	.014912	16	.014636
H_2	3.244	.002419	2.771	.002535
OH	4.037	.003010	3.495	.003197
H	1.324	.000987	1.224	.001120
O_2	2.262	.001686	1.984	.001815
O	.994	.000741	.931	.000852
CO_2	9.746	.007267	7.640	.006989
CO	13.823	.010305	11.570	.010583
Total	55.430	.041327	45.615	.041726
C	23.569	.017572	19.210	.017572
H	51.849	.038657	42.261	.038658
O		.046874 103103		.046876

By repetition we can find the correct value of y which turns out to be 17.78 atmospheres. By simple linear interpolation of the two trial solutions we find y = 17.79 atmospheres and linear interpolation of the two gas compositions as given in gm. moles/gm. leads to quantities in error by about 5 in the last decimal place. These errors combine to give an error of 1 cal./gm. in the heat of reaction, a quite negligible amount, so that there is in practice no need to calculate another solution provided one value we have chosen for y is not more than 10% in error. This limit applies when T_c = 3600°K and considerably wider limits can be allowed at lower temperatures.

The exact solution is as follows

Gas	gm. moles/gm.	H.F. at C.P.	$\overline{C}^{o}_{p}$
CO_2	.007110	94052 cal./mole.	13.758 cal./mole. °K
H_2O	.014768	57802 „ „	11.620 „ „
CO	.010462	26413 „ „	8.397 „ „
H_2	.002478	-	8.030 „ „
O_2	.001754	-	8.848 „ „
OH	.003107	- 9903 „ „	8.127 „ „
H	.001054	-52002 „ „	4.968 „ „
O	.000797	-59039 „ „	4.968 „ „
Total	.041530	1666 cal./gm.	.42714 cal./~~mole.~~ Gm °K

Nett heat available for heating 1666 - 199 = 1467 cal./gm.

Heat required to raise temperature to 3600°K = 1410 cal./gm.

Owing to the rapid increase of dissociation with temperature the effective specific heat will be of the order of 1 cal./gm. °K and so the surplus of 57 cal./gm. will raise the gas temperature by only 50 or 60°K. The next stage is therefore to recompute the gas composition for a temperature of 3660°K using a slightly lower value of y, about 17 atmospheres, to allow for the increased dissociation. If the heat balance is still in error the correct value of T_c and corresponding gas composition can be obtained by interpolation. Our next step is to calculate the total entropy, including the terms due to pressure and to mixing, as given by equation (62) and using table 6.

To calculate conditions at some stage during the adiabatic expansion we choose a temperature say 2000°K and then calculate the gas composition and total pressure for two or more values of y as before. For each value of y we calculate the total entropy and then obtain by interpolation the value of y, and the corresponding gas composition and total pressure, for which the entropy is the same as for the unexpanded gas. By repetition at other temperatures, and interpolation if necessary we can then find the gas temperature and composition for any desired final pressure, usually one atmosphere. The difference between the heat of reaction and the heat content then gives the surplus enthalpy h converted into kinetic energy, the gas velocity being given by

$$\frac{v^2}{2g} = h$$

from which the specific impulse v/g may be calculated.

For the cooler conditions near the rocket exit dissociation will be small and the first method could be used but it offers no great advantage. For temperatures over 3000°K it is almost useless.

We could have shortened the working slightly by assuming a constant gas composition during the expansion. The calculated specific impulse would have been only a few percent lower but the calculated temperature at the nozzle exit would have been some 500° or so lower. The more accurate method is essential for calculating nozzle exit area.

References

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Table 1.

Calorimetric values and heats of formation from the elements

At 300°K and corrected to low pressures.

N.B. The elementary form of carbon is taken to be graphite.

Substance	Formula	Mol. wt.	Atomic composition gm. atoms/gm.				Cal.val. cal./gm.	Heat of formation cal./gm.	
			C	H	N	O	const. vol.	const. vol.	const. pr.
Nitrocellulose	11.5% N		.023334	.030681	.008210	.035864	800	668	690
(For British	12.0		.022740	.029333	.008567	.036083	870	636	658
propellants	12.2		.022502	.028794	.008709	.036170	898	624	646
add 0.10 to the	12.3		.022383	.028525	.008781	.036214	912	618	640
nominal % N)	12.4		.022264	.028255	.008852	.036258	926	612	634
	12.6		.022026	.027716	.008995	.036345	954	599	622
	12.8		.021789	.027177	.009138	.036433	982	587	609
	13.0		.021551	.026638	.009280	.036520	1010	574	596
	13.1		.021432	.026369	.009352	.036564	1024	568	590
	13.2		.021313	.026099	.009423	.036607	1038	562	584
	13.3		.021194	.025832	.009495	.036651	1052	556	578
	13.5		.020957	.025290	.009637	.036739	1080	543	565
Nitroglycerin	$C_3H_5N_3O_9$	227.09	.013210	.022017	.013210	.039631	1750	383	405
D.E.G.D.N.	$C_4H_8N_2O_7$	196.12	.020396	.040791	.010198	.035692	1050	525	551
Dinitroglycol	$C_2H_4N_2O_6$	152.07	.013152	.026304	.013152	.039456	1740	384	408
Picrite	$C\ H_4N_4O_2$	104.07	.009609	.038434	.038434	.019217	715	189	218
Guanidine nitrate	$CH_6N_4O_3$	122.09	.008191	.049144	.032763	.024572	610	713	745
Oxamide	$C_2H_4N_2O_2$	88.07	.022710	.045419	.022710	.022710	-745	1352	1379
Dinitrotoluene	$C_7H_6N_2O_4$	182.13	.038433	.032943	.010981	.021962	-135	52	72
T.N.T.	$C_7H_5N_3O_6$	227.13	.030819	.022013	.013208	.026416	500	27	45
Diethyl phthalate	$C_{12}H_{14}O_4$	222.23	.053998	.062997	-	.017999	-1765	782	806
Dibutyl "	$C_{16}H_{22}O_4$	278.34	.057484	.079041	-	.014371	-2070	700	728
Diamyl "	$C_{18}H_{26}O_4$	306.39	.058749	.084860	-	.013055	-2190	680	709
Carbamite	$C_{17}H_{20}N_2O$	268.35	.063351	.074531	.007453	.003727	-2440	115	141
Methyl centralite	$C_{15}H_{16}N_2O$	240.29	.062424	.066585	.008323	.004162	-2380	122	146
Akardite	$C_{13}H_{12}N_2O$	212.24	.061251	.056539	.009423	.004712	-2140	-34	-13
Mineral jelly	$C_{18}H_{38}$	254.48	.070731	.149322	-	-	-3305	428	473
Special M.J.	-	-	.070791	.148608	-	-	-3260	381	426
Diphenylamine	$C_{12}H_{11}N$	169.22	.070915	.065006	.005910	-	-2660	-224	-203
Camphor	$C_{10}H_{16}O$	152.23	.065691	.105105	-	.006569	-2670	442	475
Graphite	C	12.01	.083264	-	-	-	-3365	-21	-21
Water	H_2O	18.016	-	.111012	-	.055506	0	3740	3790
Acetone	C_3H_6O	58.08	.051655	.103309	-	.017218	-1930	989	1025
Ethyl alcohol	C_2H_6O	46.07	.043414	.130242	-	.021707	-1700	1397	1442
Ethyl ether	$C_4H_{10}O$	74.12	.053967	.134916	-	.013492	-2100	814	858
T.N.T.	$C_7H_5N_3O_6$	227.13	.030819	.022013	.013208	.026416	500	27	45
Tetryl	$C_7H_5N_5O_8$	287.15	.024378	.017413	.017413	.027860	930	-46	-28
R.D.X.	$C_3H_6N_6O_6$	222.13	.013506	.027012	.027012	.027012	1360	-89	-65
P.E.T.N.	$C_5H_8N_4O_{12}$	316.15	.015815	.025305	.012652	.037957	1535	379	401
Methyl nitrate	CH_3NO_3	77.04	.012980	.038940	.012980	.038940	1640	456	483
Ethyl nitrate	$C_2H_5NO_3$	91.07	.021962	.054904	.010981	.032942	850	476	505
Nitromethane	CH_3NO_2	61.04	.016382	.049146	.016382	.032764	1120	421	450
Nitropropane	$C_3H_7NO_2$	89.09	.033672	.078569	.011224	.022448	-305	448	482
Hydrogen peroxide	85%, water 15%		-	.066628	-	.058302	748	3180	3207
Nitric acid	HNO_3	63.02	-	.015869	.015869	.047607	2547	661	685
Liquid oxygen	O_2	32.00	-	-	-	.062500	4133	78	96
Decane	$C_{10}H_{22}$	142.28	.070286	.154629	-	-	-3319	460	506
Diamond			.083264	-	-	-		38	38

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Table 2.

Heats of Formation of Explosion Products

In calories per mole corrected to low pressure.

Substance	Mol. wt.	$-\Delta H^f$	$-\Delta E^f$	
		T = 300°K	T = 300°K	T = 0°K
CO_2	44.010	94052	94052	93969
CO	28.010	26413	26711	27202
H_2O liquid	18.016	68303	67409	-
H_2O gas	18.016	57802	57504	57105
OH	17.008	-9903	-9903	-9306
NO	30.008	-21600	-21600	-21475
H	1.008	-52002	-51794	-51620
N	14.008	-85568	-85270	-85120
O	16.000	-59039	-58741	-58590
CH_4	16.042	17903	17307	15987
NH_3	17.032	10448	10150	9431

Table 3.

Free energy functions $(H_0^\circ - F^\circ)/T$ at one atmosphere pressure

In cal./mole °K

T	CO_2	H_2O	CO	H_2	N_2	O_2	OH	NO	Graphite	CH_4	NH_3
300	43.605	37.226	40.391	24.465	38.859	42.103	36.860	43.015	.523	36.505	38.185
400	45.831	39.514	42.393	26.422	40.861	44.111	38.905	45.123	.825	38.852	40.527
500	47.662	41.300	43.947	27.950	42.415	45.676	40.484	46.753	1.146	40.750	42.399
600	49.240	42.774	45.222	29.203	43.688	46.967	41.773	48.084	1.477	42.389	43.977
700	50.638	44.033	46.308	30.265	44.768	48.072	42.861	49.212	1.810	43.859	45.361
800	51.896	45.138	47.255	31.186	45.711	49.043	43.805	50.197	2.138	45.210	46.603
900	53.046	46.127	48.098	32.002	46.550	49.911	44.638	51.071	2.459	46.471	47.736
1000	54.108	47.025	48.859	32.736	47.306	50.697	45.385	51.861	2.771	47.662	48.785
1100	55.094	47.849	49.555	33.402	47.995	51.416	46.063	52.581	3.073	48.794	49.764
1200	56.017	48.613	50.196	34.012	48.629	52.079	46.685	53.243	3.365	49.873	50.686
1300	56.883	49.326	50.790	34.575	49.218	52.695	47.260	53.855	3.647	50.909	51.560
1400	57.700	49.996	51.344	35.100	49.768	53.270	47.795	54.426	3.919	51.905	52.391
1500	58.474	50.630	51.864	35.592	50.283	53.809	48.296	54.962	4.181	52.863	53.184
1600	59.209	51.231	52.354	36.055	50.769	54.317	48.766	55.466			
1700	59.910	51.803	52.818	36.492	51.229	54.798	49.210	55.942			
1800	60.580	52.350	53.259	36.905	51.666	55.254	49.632	56.395			
1900	61.221	52.874	53.678	37.297	52.082	55.688	50.034	56.826			
2000	61.835	53.376	54.078	37.671	52.478	56.103	50.416	57.237	O	H	N
2100	62.425	53.863	54.460	38.029	52.857	56.500	50.781	57.629	43.251	32.122	41.344
2200	62.993	54.331	54.826	38.373	53.220	56.880	51.132	58.005	43.486	32.353	41.575
2300	63.540	54.783	55.178	38.703	53.569	57.245	51.470	58.365	43.711	32.574	41.796
2400	64.067	55.219	55.517	39.021	53.904	57.597	51.794	58.711	43.927	32.786	42.008
2500	64.576	55.642	55.843	39.328	54.227	57.936	52.106	59.045	44.133	32.988	42.211
2600	65.069	56.053	56.157	39.625	54.539	58.263	52.408	59.366	44.330	33.183	42.406
2700	65.547	56.452	56.461	39.912	54.840	58.579	52.701	59.676	44.521	33.371	42.594
2800	66.010	56.839	56.755	40.189	55.131	58.885	52.983	59.976	44.704	33.551	42.774
2900	66.459	57.216	57.039	40.458	55.413	59.181	53.256	60.266	44.882	33.726	42.949
3000	66.896	57.583	57.314	40.719	55.686	59.468	53.522	60.548	45.054	33.894	43.117
3100	67.320	57.941	57.581	40.973	55.951	59.748	53.781	60.822	45.219	34.057	43.280
3200	67.732	58.290	57.841	41.220	56.209	60.021	54.033	61.088	45.378	34.215	43.438
3300	68.134	58.631	58.094	41.460	56.460	60.286	54.277	61.346	45.533	34.368	43.592
3400	68.526	58.964	58.340	41.694	56.704	60.544	54.514	61.597	45.683	34.516	43.740
3500	68.907	59.288	58.579	41.922	56.941	60.794	54.744	61.841	45.829	34.660	43.884
3600	69.279	59.605	58.811	42.145	57.172	61.038	54.969	62.078	45.971	34.800	44.025
3700	69.642	59.915	59.038	42.363	57.398	61.276	55.190	62.309	46.109	34.936	44.161
3800	69.996	60.219	59.260	42.576	57.618	61.508	55.406	62.534	46.244	35.069	44.294
3900	70.343	60.517	59.477	42.784	57.833	61.735	55.617	62.753	46.375	35.198	44.425
4000	70.683	60.809	59.688	42.988	58.043	61.958	55.823	62.967	46.504	35.323	44.551
4500	72.273	62.189	60.674	43.942	59.024	63.002	56.790	63.967	47.098	35.908	45.142
5000	73.714	63.445	61.566	44.809	59.910	63.947	57.667	64.868	47.635	36.432	45.675

Table 4.

Equilibrium Constants

For partial pressures expressed in atmospheres.

T °K	K_0	log K_1	log K_2	log K_3	log K_4	log K_5	log K_6	log K_7	log K_8	log K_9
300	$1.118 . 10^{-5}$	$\overline{36}.6293$	$\overline{46}.2130$	$\overline{55}.1207$	$\overline{60}.6673$	$\overline{80}.1653$	$\overline{80}.4225$	24.696	2.9491	$\overline{21}.1881$
400	$6.78 . 10^{-4}$							15.611	$\overline{}.8831$	$\overline{14}.7163$
500	.00763	$\overline{21}.8451$	$\overline{27}.8479$	$\overline{32}.3183$	$\overline{35}.6372$	$\overline{46}.3458$	$\overline{46}.2264$	10.060	$\overline{1}.5910$	$\overline{9}.2486$
600	.03704							6.298	$\overline{2}.7034$	$\overline{6}.2709$
700	.1113							3.5723	$\overline{2}.0466$	$\overline{4}.4261$
800	.2486							$\overline{1}.5074$	$\overline{3}.5430$	$\overline{2}.0375$
900	.4566							$\overline{1}.8870$	$\overline{3}.1452$	$\overline{1}.2854$
1000	.7316	$\overline{9}.3560$	$\overline{12}.7048$	$\overline{15}.8685$	$\overline{16}.4580$	$\overline{20}.2164$	$\overline{21}.8737$	$\overline{2}.5817$	$\overline{4}.8222$	0.2784
1100	1.065							$\overline{3}.5087$	$\overline{4}.5551$	1.0870
1200	1.443							$\overline{4}.6116$	$\overline{4}.3312$	1.7570
1300	1.852							$\overline{5}.8518$	$\overline{4}.1412$	2.3200
1400	2.281							$\overline{5}.1998$	$\overline{5}.9774$	2.7992
1500	2.718	$\overline{5}.2448$	$\overline{7}.7032$	$\overline{9}.7817$	$\overline{10}.7740$	$\overline{12}.9351$	$\overline{12}.5465$	$\overline{6}.6340$	$\overline{5}.8349$	3.2118
1600	3.154							$\overline{6}.1392$	$\overline{5}.7100$	3.5702
1700	3.584	$\overline{4}.1670$						$\overline{7}.7034$	$\overline{5}.6002$	3.8840
1800	4.004	$\overline{4}.5526$						$\overline{7}.3175$	$\overline{5}.5033$	4.1608
1900	4.411	$\overline{4}.8984$						$\overline{8}.9739$	$\overline{5}.4173$	4.4066
2000	4.803	$\overline{3}.2100$	$\overline{4}.2121$	$\overline{6}.7551$	$\overline{7}.9470$	$\overline{7}.3232$	$\overline{8}.9155$	$\overline{8}.6655$	$\overline{5}.3403$	4.6262
2100	5.177	$\overline{3}.4924$	$\overline{4}.5706$							
2200	5.533	$\overline{3}.7496$	$\overline{4}.8968$							
2300	5.870	$\overline{3}.9848$	$\overline{3}.1947$							
2400	6.188	$\overline{2}.2006$	$\overline{3}.4678$	$\overline{4}.2453$						
2500	6.488	$\overline{2}.3993$	$\overline{3}.7191$	$\overline{4}.5438$	$\overline{5}.8584$	$\overline{5}.9658$	$\overline{5}.5469$	$\overline{9}.5046$	$\overline{5}.0512$	5.4410
2600	6.769	$\overline{2}.5831$	$\overline{3}.9511$	$\overline{4}.8191$	$\overline{4}.1531$	$\overline{4}.3730$				
2700	7.033	$\overline{2}.7535$	$\overline{2}.1659$	$\overline{3}.0741$	$\overline{4}.4263$	$\overline{4}.7503$	$\overline{4}.2382$			
2800	7.279	$\overline{2}.9119$	$\overline{2}.3652$	$\overline{3}.3110$	$\overline{4}.6799$	$\overline{3}.1008$	$\overline{4}.6771$			
2900	7.509	$\overline{1}.0596$	$\overline{2}.5507$	$\overline{3}.5316$	$\overline{4}.9164$	$\overline{3}.4275$	$\overline{3}.0020$			
3000	7.723	$\overline{1}.1975$	$\overline{2}.7240$	$\overline{3}.7376$	$\overline{3}.1372$	$\overline{3}.7325$	$\overline{3}.3053$	$\overline{10}.7469$	$\overline{6}.8654$	5.9570
3100	7.923	$\overline{1}.3266$	$\overline{2}.8862$	$\overline{3}.9304$	$\overline{3}.3438$	$\overline{2}.0178$	$\overline{3}.5894$			
3200	8.112	$\overline{1}.4479$	$\overline{1}.0382$	$\overline{2}.1111$	$\overline{3}.5377$	$\overline{2}.2852$	$\overline{3}.8559$			
3300	8.290	$\overline{1}.5619$	$\overline{1}.1807$	$\overline{2}.2807$	$\overline{3}.7200$	$\overline{2}.5364$	$\overline{2}.1062$			
3400	8.455	$\overline{1}.6693$	$\overline{1}.3147$	$\overline{2}.4403$	$\overline{3}.8916$	$\overline{2}.7729$	$\overline{2}.3418$			
3500	8.606	$\overline{1}.7706$	$\overline{1}.4411$	$\overline{2}.5910$	$\overline{2}.0535$	$\overline{2}.9962$	$\overline{2}.5643$	$\overline{10}.2187$	$\overline{6}.7380$	
3600	8.744	$\overline{1}.8663$	$\overline{1}.5606$	$\overline{2}.7334$	$\overline{2}.2065$	$\overline{1}.2074$	$\overline{2}.7747$			
3700	8.872	$\overline{1}.9570$	$\overline{1}.6738$	$\overline{2}.8680$	$\overline{2}.3514$	$\overline{1}.4073$	$\overline{2}.9738$			
3800	8.994	0.0430	$\overline{1}.7811$	$\overline{2}.9953$	$\overline{2}.4888$	$\overline{1}.5967$	$\overline{1}.1622$			
3900	9.107	0.1246	$\overline{1}.8828$	$\overline{1}.1159$	$\overline{2}.6193$	$\overline{1}.7764$	$\overline{1}.3409$			
4000	9.208	0.2019	$\overline{1}.9793$	$\overline{1}.2305$	$\overline{2}.7432$	$\overline{1}.9474$	$\overline{1}.5112$	$\overline{11}.8305$	$\overline{6}.6459$	
4500	9.632	0.5389	0.3864	$\overline{1}.7259$	$\overline{1}.2820$	0.6865	0.2465	$\overline{11}.5394$	$\overline{6}.5780$	
5000	9.902	0.8094	0.7309	0.1226	$\overline{1}.7150$	1.2807	0.8377	$\overline{11}.3108$	$\overline{6}.5264$	

N.B. For explanation see next page.

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Explanation of Table 4.

$$K_0 = \frac{p(CO) \cdot p(H_2O)}{p(CO_2) \cdot p(H_2)} \quad \text{or} \quad \frac{(CO) \cdot (H_2O)}{(CO_2) \cdot (H_2)}$$

$K_1 = p(H)/\surd\{p(H_2)\}$

$K_2 = p(OH)\ \surd\{p(H_2)\}/p(H_2O)$

$K_3 = p(NO) \cdot p(H_2)/p(H_2O)\ \surd\{p(N_2)\}$

$K_4 = p(N)/\surd\{p(N_2)\}$

$K_5 = p(O) \cdot p(H_2)/p(H_2O)$

$K_6 = p(O_2) \cdot \{p(H_2)/p(H_2O)\}^2$

$K_7 = p(CH_4) \cdot p(H_2O)/p(CO)\ \{p(H_2)\}^3$

$K_8 = p(NH_3)/\surd\{p(N_2)\} \cdot \{p(H_2)\}^{3/2}$

$K_9 = \{p(CO)\}^2/p(CO_2)$ in presence of graphite.

The gases are assumed perfect in all cases.

Table 5.

Mean Specific Heats $\overline{C_v}$ between 300 and T °K at Constant Volume

In cal./mole °K

T °K	CO_2	H_2O	CO	H_2	N_2	O_2	OH	NO	Graphite	CH_4	NH_3
0	5.527	5.950	4.964	4.801	4.963	4.955	5.077	5.377	.851	6.052	6.080
300	6.904	6.042	4.978	4.908	4.974	5.032	5.153	5.158	2.083	6.586	6.521
400	7.412	6.115	4.996	4.958	4.986	5.110	5.112	5.159	2.473	7.134	6.843
500	7.853	6.212	5.035	4.978	5.013	5.220	5.091	5.195	2.828	7.799	7.208
600	8.238	6.328	5.093	4.987	5.056	5.334	5.081	5.265	3.143	8.497	7.581
700	8.576	6.452	5.164	5.000	5.113	5.448	5.080	5.346	3.417	9.192	7.951
800	8.876	6.586	5.241	5.015	5.180	5.556	5.090	5.429	3.653	9.866	8.315
900	9.145	6.725	5.321	5.033	5.251	5.656	5.108	5.513	3.855	10.510	8.671
1000	9.385	6.868	5.400	5.055	5.323	5.747	5.131	5.594	4.027	11.122	9.016
1100	9.601	7.013	5.477	5.082	5.395	5.829	5.160	5.670	4.175	11.700	9.349
1200	9.796	7.159	5.549	5.114	5.465	5.903	5.196	5.741	4.306	12.243	9.669
1300	9.972	7.304	5.617	5.150	5.532	5.971	5.240	5.807	4.425	12.752	9.975
1400	10.132	7.448	5.681	5.188	5.595	6.033	5.288	5.868	4.533	13.228	10.268
1500	10.278	7.589	5.741	5.228	5.654	6.091	5.336	5.925	4.632	13.672	10.546
1600	10.411	7.726	5.797	5.270	5.710	6.144	5.383	5.977		14.089	10.811
1700	10.533	7.860	5.849	5.313	5.763	6.194	5.430	6.025		14.477	11.062
1800	10.645	7.989	5.897	5.357	5.813	6.241	5.475	6.068		14.840	11.299
1900	10.748	8.115	5.942	5.401	5.860	6.286	5.519	6.108		15.180	11.524
2000	10.844	8.236	5.984	5.445	5.903	6.328	5.562	6.146		15.497	11.737
2100	10.933	8.352	6.024	5.489	5.943	6.369	5.604	6.182			
2200	11.015	8.464	6.061	5.532	5.981	6.409	5.645	6.216			
2300	11.092	8.572	6.096	5.574	6.017	6.447	5.686	6.248			
2400	11.164	8.674	6.128	5.615	6.051	6.484	5.727	6.278			
2500	11.231	8.773	6.159	5.656	6.083	6.520	5.767	6.306		16.819	12.644
2600	11.295	8.868	6.189	5.696	6.114	6.555	5.809	6.332			
2700	11.355	8.959	6.217	5.735	6.143	6.589	5.846	6.357			
2800	11.411	9.046	6.243	5.773	6.171	6.622	5.884	6.381			
2900	11.464	9.130	6.267	5.810	6.197	6.654	5.920	6.404			
3000	11.514	9.210	6.290	5.846	6.221	6.685	5.955	6.425	6.0	17.807	13.343
3100	11.562	9.288	6.312	5.881	6.245	6.716	5.988	6.445			
3200	11.608	9.362	6.334	5.915	6.268	6.746	6.021	6.465			
3300	11.651	9.434	6.355	5.948	6.290	6.776	6.053	6.484			
3400	11.693	9.503	6.374	5.981	6.310	6.805	6.083	6.503			
3500	11.733	9.569	6.392	6.013	6.329	6.833	6.112	6.521		18.570	13.893
3600	11.771	9.633	6.410	6.043	6.348	6.861	6.140	6.536			
3700	11.807	9.694	6.427	6.072	6.366	6.889	6.168	6.552			
3800	11.842	9.753	6.444	6.101	6.383	6.916	6.195	6.567			
3900	11.876	9.810	6.460	6.129	6.400	6.942	6.221	6.582			
4000	11.908	9.864	6.475	6.156	6.416	6.968	6.246	6.597		19.175	14.337
4500	12.053	10.110	6.542	6.285	6.490	7.084	6.372	6.668		19.667	14.701
5000	12.177	10.310	6.602	6.398	6.548	7.191	6.482	6.730		20.075	15.007

For monatomic gases take $\overline{C_v}$ = 2.981.
To obtain $\overline{C_p}$ add 1.987.

<u>Table 6.</u>

Entropies at One Atmosphere Pressure

In cal./mole °K

T °K	CO_2	H_2O	CO	H_2	N_2	O_2	OH	NO	Graphite	CH_4	NH_3
300	51.119	45.162	47.342	31.253	45.809	49.045	43.924	50.379	1.374	45.078	46.252
400	53.816	47.492	49.352	33.250	47.818	51.092	45.978	52.433	2.081	48.600	48.785
500	56.107	49.342	50.927	34.809	49.385	52.724	47.554	54.044	2.788	51.917	50.917
600	58.110	50.900	52.238	36.084	50.685	54.099	48.839	55.392	3.474	54.975	52.795
700	59.893	52.257	53.373	37.167	51.805	55.296	49.927	56.558	4.127	57.782	54.497
800	61.503	53.472	54.379	38.108	52.797	56.361	50.878	57.593	4.740	60.364	56.067
900	62.972	54.581	55.287	38.945	53.692	57.321	51.723	58.526	5.313	62.743	57.531
1000	64.323	55.605	56.115	39.702	54.509	58.194	52.487	59.377	5.846	64.938	58.907
1100	65.572	56.559	56.878	40.395	55.260	58.994	53.188	60.158	6.342	66.963	60.208
1200	66.733	57.456	57.586	41.035	55.956	59.732	53.838	60.880	6.807	68.835	61.445
1300	67.817	58.304	58.245	41.631	56.606	60.418	54.450	61.550	7.247	70.570	62.624
1400	68.833	59.110	58.860	42.192	57.215	61.059	55.025	62.176	7.663	72.182	63.749
1500	69.789	59.878	59.437	42.722	57.786	61.660	55.567	62.764	8.057	73.682	64.824
1600	70.692	60.611	59.982	43.224	58.326	62.226	56.079	63.318			
1700	71.547	61.313	60.498	43.702	58.838	62.761	56.565	63.840			
1800	72.359	61.986	60.988	44.157	59.325	63.268	57.028	64.335			
1900	73.132	62.634	61.453	44.591	59.788	63.751	57.470	64.806			
2000	73.869	63.258	61.896	45.007	60.228	64.212	57.892	65.255	O	H	N
2100	74.573	63.859	62.320	45.407	60.647	64.654	58.297	65.684	48.219	37.090	46.312
2200	75.247	64.439	62.726	45.792	61.049	65.078	58.687	66.094	48.454	37.321	46.543
2300	75.893	64.999	63.114	46.163	61.435	65.485	59.064	66.487	48.679	37.542	46.764
2400	76.513	65.540	63.486	46.521	61.806	65.877	59.427	66.864	48.895	37.754	46.976
2500	77.110	66.064	63.845	46.868	62.163	66.255	59.778	67.226	49.101	37.956	47.179
2600	77.686	66.571	64.191	47.204	62.507	66.621	60.119	67.575	49.298	38.151	47.374
2700	78.242	67.063	64.525	47.530	62.839	66.974	60.448	67.911	49.489	38.339	47.562
2800	78.779	67.540	64.847	47.845	63.160	67.315	60.767	68.236	49.672	38.518	47.742
2900	79.298	68.004	65.158	48.151	63.470	67.646	61.076	68.551	49.850	38.694	47.917
3000	79.800	68.455	65.459	48.448	63.770	67.968	61.376	68.856	50.022	38.862	48.085
3100	80.286	68.894	65.751	48.737	64.060	68.282	61.668	69.151	50.187	39.025	48.248
3200	80.758	69.321	66.034	49.018	64.342	68.587	61.952	69.438	50.346	39.183	48.406
3300	81.216	69.736	66.309	49.291	64.616	68.884	62.228	69.717	50.501	39.336	48.560
3400	81.662	70.140	66.576	49.558	64.882	69.172	62.495	69.988	50.651	39.484	48.708
3500	82.096	70.533	66.835	49.818	65.141	69.453	62.755	70.251	50.797	39.628	48.852
3600	82.517	70.917	67.087	50.072	65.392	69.727	63.009	70.506	50.939	39.768	48.993
3700	82.927	71.292	67.333	50.319	65.637	69.995	63.257	70.753	51.077	39.904	49.129
3800	83.326	71.659	67.573	50.561	65.876	70.256	63.500	70.994	51.212	40.037	49.262
3900	83.716	72.018	67.808	50.798	66.110	70.511	63.737	71.230	51.343	40.166	49.393
4000	84.099	72.368	68.037	51.030	66.338	70.762	63.969	71.460	51.472	40.291	49.519
4500	85.878	74.008	69.100	52.115	67.402	71.931	65.063	72.536	52.066	40.876	50.110
5000	87.479	75.481	70.056	53.099	68.351	72.991	66.052	73.504	52.603	41.400	50.643

Table 7.

Specific Heats C_v at Constant Volume

In cal./mole °K

T °K	CO_2	H_2O	CO	H_2	N_2	O_2	OH	NO	Graphite	CH_4	NH_3
300	6.904	6.042	4.978	4.908	4.974	5.032	5.153	5.158	2.083	6.586	6.521
400	7.885	6.202	5.026	4.987	5.004	5.207	5.086	5.180	2.851	7.761	7.196
500	8.672	6.430	5.133	5.006	5.083	5.432	5.061	5.305	3.506	9.179	7.949
600	9.316	6.695	5.289	5.021	5.210	5.683	5.064	5.486	4.030	10.599	8.700
700	9.850	6.974	5.464	5.048	5.364	5.898	5.099	5.673	4.440	11.936	9.423
800	10.296	7.267	5.637	5.091	5.526	6.077	5.162	5.848	4.750	13.166	10.115
900	10.668	7.569	5.800	5.152	5.684	6.225	5.247	6.006	4.980	14.284	10.772
1000	10.979	7.873	5.945	5.230	5.829	6.348	5.346	6.140	5.140	15.288	11.390
1100	11.241	8.175	6.071	5.320	5.960	6.453	5.454	6.255	5.280	16.182	11.965
1200	11.462	8.468	6.181	5.417	6.076	6.543	5.566	6.354	5.420	16.974	12.493
1300	11.649	8.749	6.277	5.518	6.177	6.621	5.676	6.438	5.560	17.673	12.974
1400	11.808	9.015	6.360	5.622	6.266	6.690	5.784	6.509	5.680	18.290	13.410
1500	11.945	9.263	6.432	5.726	6.344	6.752	5.888	6.571	5.760	18.832	13.804
1600	12.064	9.494	6.494	5.827	6.413	6.811	5.986	6.625			
1700	12.167	9.707	6.548	5.924	6.473	6.868	6.078	6.673			
1800	12.257	9.903	6.597	6.017	6.526	6.925	6.163	6.715			
1900	12.337	10.084	6.640	6.105	6.573	6.981	6.243	6.753			
2000	12.408	10.250	6.678	6.188	6.615	7.037	6.318	6.787			
2100	12.471	10.403	6.712	6.267	6.653	7.093	6.388	6.816	For monatomic gases take $C_v = 2.981$. To obtain C_p add 1.987.		
2200	12.528	10.544	6.743	6.341	6.687	7.150	6.453	6.842			
2300	12.580	10.675	6.771	6.411	6.718	7.208	6.514	6.866			
2400	12.627	10.795	6.797	6.477	6.746	7.265	6.571	6.888			
2500	12.670	10.905	6.821	6.539	6.772	7.318	6.625	6.909			
2600	12.710	11.007	6.843	6.598	6.796	7.365	6.675	6.928			
2700	12.747	11.102	6.863	6.654	6.818	7.408	6.723	6.946			
2800	12.781	11.189	6.881	6.707	6.839	7.450	6.768	6.962			
2900	12.813	11.269	6.897	6.757	6.858	7.491	6.811	6.978			
3000	12.843	11.344	6.912	6.804	6.875	7.531	6.852	6.993			
3100	12.871	11.413	6.926	6.848	6.891	7.571	6.891	7.008			
3200	12.898	11.478	6.940	6.890	6.906	7.611	6.928	7.022			
3300	12.924	11.538	6.953	6.930	6.920	7.651	6.963	7.035			
3400	12.949	11.593	6.965	6.969	6.934	7.687	6.997	7.048			
3500	12.972	11.645	6.976	7.006	6.947	7.724	7.030	7.061			
3600	12.995	11.693	6.987	7.041	6.959	7.760	7.061	7.074			
3700	13.017	11.737	6.998	7.074	6.970	7.795	7.091	7.086			
3800	13.038	11.777	7.008	7.105	6.981	7.829	7.120	7.097			
3900	13.059	11.814	7.018	7.135	6.992	7.861	7.148	7.109			
4000	13.079	11.847	7.028	7.164	7.002	7.892	7.174	7.120			
4500	13.174	11.974	7.072	7.295	7.049	8.016	7.343	7.172			
5000	13.264	11.986	7.112	7.402	7.089	8.128	7.518	7.221			

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