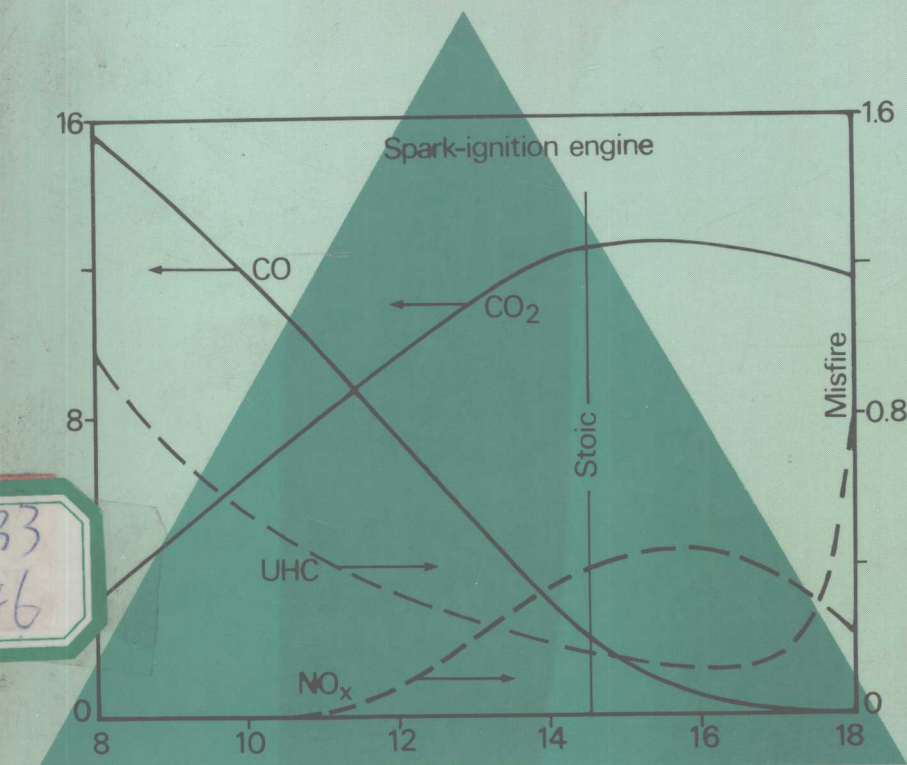# Combustion Calculations

THEORY, WORKED EXAMPLES AND PROBLEMS

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COMBUSTION CALCULATIONS
Theory, worked examples and problems

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M

iv

PREFACE

Examination syllabuses concerned with combustion reactions and their products tend to draw on material appearing in texts on chemistry, physics, thermodynamics, fuel science and the few publications devoted to combustion itself. Furthermore, some aspects of the subject tend to be handled in a 'case law' manner by depending solely on worked examples to illustrate the techniques of solution, whereas a prior general statement of the relevant theory permits much wider application.

The objectives of this present book, therefore, are threefold.

(1) To assemble in one small volume the key relationships of stoichiometry, thermochemistry and kinetics that apply to the calculation of combustion quantities.

(2) To unify these relationships by starting with a general combustion equation, in simple terms of molecular products only, and adapting this systematically to each aspect in turn.

(3) To provide solutions in general terms before illustrating their use in examples typical of examination questions met in combustion and allied fields.

The motivation for a work of this kind stemmed from experience with examination marking at H.N.C., H.N.D. and first- and higher-degree levels in various branches of engineering and fuel technology, where it has become apparent that questions of this type present difficulties to some candidates. This approach can also serve in professional practice as a reminder of the basic principles involved before turning to the more sophisticated instrumentation and computational techniques available in industry and research.

The book opens with a brief review of the main features of atmospheric air and conventional fuels, together with those of the most common combustion products and their methods of measurement. The following chapter deals with the determination of the proportions of reactants, and of the cooled, stable products of combustion. Chapter 5 is concerned with the determination of proportions of hot products that are still reacting but have reached some condition of dynamic equilibrium. Chapter 6 deals with the quantities of energy involved in combustion reactions, and chapter 7 with the temperatures reached under adiabatic, or some other specified, conditions. The efficiency of combustion is covered in chapter 8, whereas chapter 9 indicates the enhanced efficiency realised by electrochemical oxidation in the absence of substantial heat release. All key equations are numbered in sequence, and listed in a final summary. As a general rule, decimal fractions are used, but it has occasionally proved more convenient to include such a term as $(x + y/4)$ rather than $(x + 0.25y)$. Worked examples are included at the

ends of chapters, and a number of problems provided, with answers. SI units are used throughout, and extracts from the wealth of thermo-chemical data published in kcal/mol have been converted by the relationship

$$(X) \text{ kcal/mol} = 4.184(X) \text{ kJ/mol}$$

Cranfield, 1976   E. M. GOODGER

UNITS

In any system of units, certain quantities are defined as basic to the system, and all further quantities derived from them. If the system is coherent, the products and quotients of any two or more unit quantities themselves become the units of the derived quantities. Thus, in the case of Newton's second law, F = ma, 1 derived unit of force is equal to

(1 unit of mass) × (1 unit of length)/(1 unit of time)^2

One of the most significant developments in this area is the adoption of a rationalised system of metric units known as SI (Système International d'Unités), which is coherent, with a derived unit of energy common to the mechanical, electrical and most other forms. SI includes the following base units

length	metre (m)
mass	kilogram (kg)
time	second (s)
electric current	ampere (A)
thermodynamic temperature	kelvin (K)
amount of substance	mole (mol)

It should be noted that the kelvin is also used for temperature intervals, and that the mole relates to what was formerly called the 'gram-mole' and not the 'kilogram-mole' (kmol).

SI includes the following derived units

force	newton (N) = kg m/s^2
pressure	pascal (Pa) = N/m^2 = kg/m s^2
energy	joule (J) = N m = kg m^2/s^2
power	watt (W) = J/s = kg m^2/s^3

No change is made to any symbol to indicate the plural.

SI has been adopted by various industries (for example, *Recommended SI Units,* Institute of Petroleum, London, 1970), some of which also use earlier metric units such as the litre and the bar, which are not part of SI but are considered acceptable. Since the adoption of SI is not yet worldwide, the following conversion factors and other metric relationships are given.

length	1 ft = 0.3048 m
volume	1 ft^3 = 0.028 32 m^3
	1 U.K. gal = 1.201 U.S. gal = 4.546 litre
mass	1 lb = 0.4536 kg
	1 tonne = 1000 kg
density	1 lb/ft^3 = 16.0185 kg/m^3

force	1 lbf = 4.4482 N
pressure	1 lbf/in.^{2} = 6.894 76 kPa
	1 mm Hg = 133.322 Pa
	1 atm = 101.325 kPa = 1.01325 bar
	1 bar = 100 kPa = 10^5 Pa
energy	1 Btu = 1.0551 kJ
	1 Chu = 1.8991 kJ
	1 kcal (international table) = 4.1868 kJ
	1 kcal (thermochemical) = 4.184 kJ
	1 kWh = 3.6 MJ
	1 hp h = 2.6845 MJ
	1 therm = 10^5 Btu = 105.51 MJ
specific energy	1 Btu/lb = 2.326 kJ/kg
specific energy capacity	1 Btu/lb $^\circ$R = 1 Chu/lb K = 4.1868 kJ/kg K
volumetric energy	1 Btu/ft^3 = 0.0373 kJ/litre (or MJ/m^3)
	1 Btu/U.K. gal = 0.232 kJ/litre (or MJ/m^3)
power	1 hp = 745.7 W

NOTATION

When two symbols are given for one item, upper case represents an extensive property (dependent on mass) and lower case a specific property (per unit mass). When one symbol is used for more than one item, the particular meaning in any instance will be apparent from the context.

A   air mass

A, a   non-flow availability function

$\dot{A}$ air mass flow rate

A/F   air/fuel ratio by mass or by volume

B, b   steady-flow availability function

C   molar heat capacity

c   specific heat capacity

C/H   carbon/hydrogen mass ratio

CV   calorific value

E   electrical potential

e   charge/electron

F   fuel mass

$\dot{F}$ fuel mass flow rate

G, g   Gibbs free-energy function

(g)   gas

GCV   gross calorific value

(gr)   graphite

H, h   enthalpy

i   electrical current

ip   indicated power

K   equilibrium constant

k   rate constant

(1)	liquid
M	number of moles of oxygen/gram of fuel
m	number of moles of oxygen/mole of fuel
$\dot{m}$	mass consumption rate
NCV	net calorific value
n	number of moles of a combustion product/mole of fuel
n-f	non-flow
p	pressure
Q, q	heat transfer (note: not a property)
R_0	universal gas constant
RAM	relative atomic mass (formerly atomic weight)
RMM	relative molecular mass (formerly molecular weight)
r	ratio
S, s	entropy
(s)	solid
s-f	steady-flow
T	absolute thermodynamic temperature (K)
t	empirical temperature (^{o}C); time
U, u	internal energy
V, v	volume
W, w	work transfer (note: not a property)
X	any oxygen-consuming component of a fuel
x	number of atoms of carbon/molecule fuel
y	number of atoms of hydrogen/molecule fuel
z	number of atoms of oxygen/molecule fuel
α	cut-off ratio in diesel cycle
γ	ratio of specific heat capacities
Δ	finite change

η	efficiency
φ	equivalence ratio

Superscripts

o	standard state of 25 ^{o}C (298.15 K) and 1 atm
'	concentration basis; theoretical; molar basis
*	algebraic sum of sensible and standard formation

Subscripts

A	air
a	atomisation
ad	adiabatic
C	change
c	combustion; corrected
cc	combustion chamber
F	fuel
f	formation
fg	saturated vapour - saturated liquid
I	initial
i	any arbitrary reactant component
j	any arbitrary product component
max	maximum
max useful	maximum useful
min	minimum
0	absolute zero temperature; environment
o	observed
P	products
p	pressure (constant)
R	reactants; reverse
r	reaction

xiii

s	stoichiometric
T	temperature (either constant, or equal initial and final); total
t	total head
V; v	volume (constant)
V	volumetric
WG	water gas

CONTENTS

I   INTRODUCTION

Combustion of mixtures of fuel with air is widely used for the con-
version of chemical energy to provide heat transfer in furnaces, or
work transfer in engines. Once the components of a fuel are known
quantitatively, straightforward calculation is possible of the
stoichiometric mixture proportions (chemically balanced for complete
reaction) with air or some other oxidant. Furthermore, if the re-
sulting products are cooled, the proportions of stable molecular
quantities are obtainable directly. Any known non-stoichiometric
reactant mixture can be handled in a similar way. In a reverse
manner, analytical data on cooled dry products of hydrocarbon com-
bustion permit calculation of the carbon/hydrogen mass ratio of the
parent fuel, and the fuel/air mass ratio of the parent mixture.

Products that are still hot, on the other hand, are unstable,
with a tendency to dissociate back towards the reactant form. In
such cases, information on combustion kinetics is also required to
establish the degree of dissociation, and the quantities of the more
complex product mixtures of molecular, atomic and radical species
are then obtainable by iteration.

The quantity of energy released as a result of combustion can be
determined as the difference between the energy stock of the final
products and that of the initial reactants, and can be expressed as
a heat transfer in terms of a calorific value of the fuel when burnt
with the oxidant under prescribed conditions. The maximum possible
energy output from the products in the form of useful work can also
be calculated. A combination of the above information permits the
derivation of the temperature reached during combustion, and of the
efficiency of the energy-conversion process. Consequently many as-
pects of the combustion performance of a fuel/oxidant mixture can
be predicted from knowledge of the nature, proportions and energy
content of the mixture components. A far more efficient process of
energy conversion is available by the indirect electrochemical reac-
tion of fuel and oxidant in a fuel cell, involving no high-tempera-
ture heat transfer at all, and this represents the ultimate in
efficiency of conversion from chemical energy to work.

TABLE 1   *RELATIVE ATOMIC AND MOLECULAR MASSES* $(C^{12} = 12)$

Element	Symbol	RAM	Approx. RAM	Compound	Symbol	RMM	Approx. RMM
Argon	Ar	39.948	40	Carbon dioxide	CO_2	44.00995	44
Carbon	C	12.01115	12	Carbon monoxide	CO	28.01055	28
Hydrogen	H	1.00797	1	Hydrogen	H_2	2.01594	2
Nitrogen	N	14.0067	14	Nitrogen	N_2	28.0134	28
Oxygen	O	15.9994	16	Oxygen	O_2	31.9988	32
Sulphur	S	32.064	32	Sulphur dioxide	SO_2	64.0628	64
				Water	H_2O	18.01534	18

2

2   COMBUSTION REACTANTS

The chemical elements and their oxides of interest in this study
are listed in table 1 together with their relative atomic and mole-
cular masses (RAM and RMM); for simplicity, approximate values
have been adopted throughout this book. Since atmospheric air is
the most common oxidant, it is also used here, and is represented
in table 2. It is seen that (m) moles of oxygen are contained in
(4.76m) moles of air, representing (32m) grams of oxygen and
(4.31 × 32m), or (137.9m), grams of air. In some advanced applica-
tions to rocket propulsion, oxygen alone, or such alternatives as
hydrogen peroxide, nitrogen oxides, nitric acid or fluorine, may be
required as the oxidant, but the following treatment can be adapted
for any oxidant provided its components, and their chemical behaviour,
are known.

TABLE 2   COMPOSITION OF ATMOSPHERIC AIR

Component	Molar Fraction	RMM	Mass Fraction
N_2	0.781	28.0134	0.756
Ar + CO_2	0.009	(40)	0.012
'Atmospheric' N_2	0.790	(28.150)	0.768
O_2	0.210	31.9988	0.232

where ( ) signifies approximate.   Thus

'atmospheric' N_2/O_2 ratio = 3.76 by volume (molar)

= 3.31 by mass

RMM air = (28.150 × 0.790) + (31.9988 × 0.210)

= 28.96 approximately, allowing for traces of
Ar and CO_2

Density of air = $\dfrac{RMM}{V_M}$

= $\dfrac{28.96}{22.4136}$ = 1.292 kg/m^3 at 1 atm and 0 °C

In their simplest form, fuels are represented by the great variety
of either natural or manufactured hydrocarbons, which are identified
individually by formulae of the C_xH_y type, where x and y are integers,

and x is known as the carbon number. Collectively, hydrocarbons are recognised as being one of a number of 'series', each member of a particular series differing slightly from its adjacent fellow members but having a general formula and structural characteristics in common. The main series range from the straight-chain saturated *paraffins* (alkanes) with y = 2x + 2, through the cyclic *naphthenes* (cyclanes or cycloparaffins) and unsaturated *olefins* (alkenes) both with y = 2x, to the highly unsaturated *acetylenes* (alkynes) with y = 2x - 2, and eventually the cyclic *aromatics*, which, in their single 'nuclear' configuration, have y = 2x - 6. The hydrogen content therefore falls progressively from paraffins to aromatics, and even further when benzene rings combine to form the *polynuclear aromatics*, as with the double ring naphthalene $C_{10}H_8$, with y = 2x - 12, and the triple ring anthracene $C_{14}H_{10}$, with y = 2x - 18.

For an individual hydrocarbon, therefore

$$RMM = (12x + y) \text{ approximately} \qquad (1)$$

and $\quad$ carbon/hydrogen mass ratio = (12x/y) approximately $\qquad$ (2)

A plot of C/H mass ratio in figure 1 shows that, with the exception of the polynuclear aromatics, values tend to 6 as x increases, since y then tends to 2x.[1]
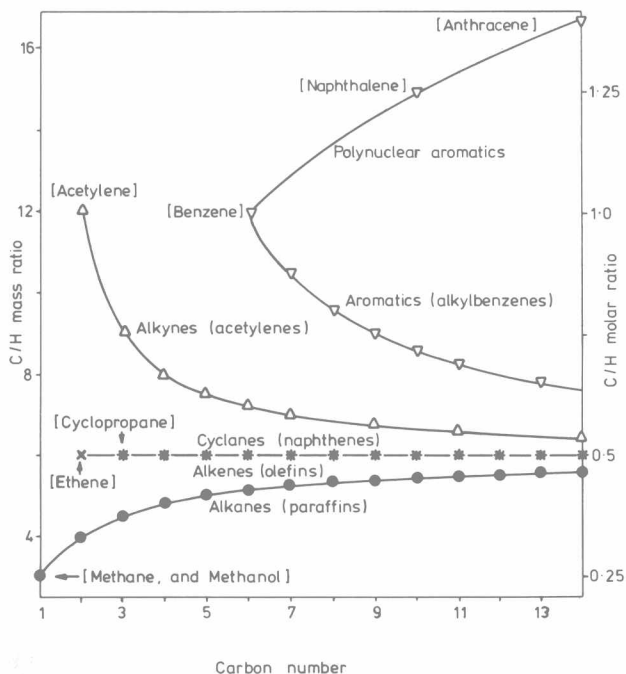

Figure 1   Carbon/hydrogen ratio of light hydrocarbons (ref. 1)

4