A New Approach to Thermochemical Calculations of Condensed Fuel-Oxidizer Mixtures

S. R. JAIN and K. C. ADIGA

Propellant Chemistry Laboratory, Department of Aeronautical Engineering, Indian Institute of Science, Bangalore 560012, India

and

V. R. PAI VERNEKER

High Energy Solids Laboratory, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India

A simple method of calculating the elemental stoichiometric coefficient, ϕ_e has been developed, which can easily be applied to multicomponent fuel-oxidizer compositions. The method correctly predicts whether a mixture is fuel lean, fuel rich, or stoichiometrically balanced. The total composition of oxidizing (or reducing) elements of the mixture appears to be related to the thermochemistry of the system. For the reaction of ammonium perchlorate and an organic fuel the heat of reaction varies linearly with the total composition of oxidizing elements. The physical significance of such a correlation based on thermochemical reasoning is highlighted in the paper.

INTRODUCTION

Simple methods for calculating thermochemical parameters of fuel-oxidizer mixtures are desirable for various purposes in the field of propellants and explosives. The constitution of a fuel-oxidizer mixture is usually expressed in terms of parameters such as mixture ratio, equivalence ratio, elemental stoichiometric coefficient, and so on. The fuel "richness" or "leanness" of a combustible mixture is usually determined by the equivalence ratio ϕ, which is defined as $\phi = \phi_s/\phi_m$, where ϕ_m is the mixture ratio (fuel/oxidizer) and ϕ_s is the stoichiometric ratio [1]. A value of $\phi > 1$ indicates that the mixture is fuel lean, whereas $\phi < 1$ shows it to be fuel rich. Although equivalence ratio rightly predicts the fuel richness or leanness of the composition, Bakhman [2] pointed out that for a given value of ϕ, different mixtures may differ substantially with respect to oxygen balance—mainly because the mixture ratio term does not take into account the intramolecular fuel and oxidizer elements present in the oxidizer and in the fuel. Another parameter called "elemental stoichiometric coefficient" ϕ_e was suggested by Bakhman which reflects the relationship between the intramolecular "fuel" and "oxidizer." Whereas $\phi_e = \phi = 1$ for stoichiometrically balanced compositions, they may differ substantially at other compositions. The deviations become more apparent when the fuel contains the "oxidizer" and the oxidizer contains "fuel" elements.

In this paper we report an easier method of calculating the elemental stoichiometric coefficient, ϕ_e which is applicable to multicomponent systems. The extension of ϕ_e calculations on systems involving ammonium perchlorate (AP)-

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organic fuels has led to other parameters which appear to be related to the energetics of such mixtures.

CALCULATION OF ϕ_e

In the present treatment, ϕ_e actually represents the ratio of the oxidizing to reducing (fuel) elemental composition. All the oxidizing and reducing elements are treated in a similar manner irrespective of whether they are present in the oxidizer or the fuel components. ϕ_e is defined as

$$\phi_e = \frac{\text{Total composition of oxidizing elements in the mixture}}{\text{Total composition of reducing elements in the mixture}}$$

$$= \frac{\Sigma \text{ Coefficient of oxidizing elements in specific formula } x \text{ valency}}{(-1)\,\Sigma \text{ Coefficient of reducing elements in specific formula } x \text{ valency}}$$

$$= \frac{p}{r},$$

where p and r are integers representing the total composition of the oxidizing and the reducing elements respectively in the mixture. A mixture is fuel rich if $\phi_e < 1$, fuel lean if $\phi_e > 1$, and stoichiometrically balanced at $\phi_e = 1$. For calculating ϕ_e the specific formulas of the oxidizer and the fuel components are first calculated. A model calculation of ϕ_e for a mixture of an oxidizer NH_4ClO_4 (AP) and a fuel, polymethylmethacrylate $(C_5H_8O_2)_n$, (PMMA) in the ratio 70:30 by weight is shown here. The valences of the oxidizing elements Cl and O have been taken as positive and those of fuel elements C and H as negative, with N taken as neutral [1].

Specific formula for 70 grams of AP

$$= \frac{N_{1\times 70}}{117.5} \cdot \frac{H_{4\times 70}}{117.5} \cdot \frac{Cl_{1\times 70}}{117.5} \cdot \frac{O_{4\times 70}}{117.5}$$

$$= N_{0.5957} \cdot H_{2.3828} \cdot Cl_{0.5957} \cdot O_{2.3828}.$$

Specific formula for 30 grams of PMMA

$$= C_{1.500} \cdot H_{2.40} \cdot O_{0.60}.$$

$$\phi_e = \frac{(0.5957 \times 1) + (2.3828 \times 2) + (0.60 \times 2)}{(-1)[(1.50 \times -4) + (2.40 \times -1) + (2.3828 \times -1)]}$$

$$= \frac{6.5613}{10.7828} = 0.6085.$$

A value of $\phi_e < 1$ in the present case means the mixture is fuel rich. When this procedure of calculation was used, ϕ_e values of other mixtures reported by Bakhman were calculated and found to be the same as those he reported. A close look at the final expression of Bakhman's procedure shows parameters identical to those in the present case. However, the present method is exceedingly simple, whereas the other method is quite tedious, involving balancing and solving of chemical equations. Furthermore, the present method can be applied with equal simplicity to systems containing more than two components. Table 1 gives ϕ_e values for various multicomponent systems at randomly selected compositions. Here again, ϕ_e values differ considerably from ϕ values.

Incidentally, it is seen that the concept of total oxidizing or reducing valences immensely helps in simplifying the balancing of chemical equations for a three-component fuel-oxidizer mixture and thus in calculating the stoichiometric composition of the mixture. For example, consider calculating the stoichiometric composition of the system NH_4ClO_4-$C_{10}H_8$-$(CH_3)NH_3NO_3$. Here, AP is fuel lean and therefore an oxidizer; whereas $C_{10}H_8$ and $CH_3NH_3NO_3$ are fuel rich and consequently are fuels. When the two fuels are taken in equimolar ratio

the total reducing valences of fuels ($C_{10}H_8$ and $CH_3NH_3NO_3$)

$$= ((10 \times -4) + (8 \times -1)) + ((1 \times -4) + (6 \times -1) + (3 \times 2))$$

$$= -52.$$

TABLE 1

ϕ_e Values for Multicomponent Systems

System No.	System	ϕ_e	ϕ
1.	Two oxidizers and one organic fuel, NH_4ClO_4 70, $KClO_4$ 5, CTPB[a] 25	0.739	0.671
2.	Two oxidizers, an organic fuel and a metal fuel NH_4ClO_4 70, $KClO_4$ 5, PMMA 12, Al 13	0.854	0.717
3.	One oxidizer, an organic fuel, and metal fuel NH_4ClO_4 75, PMMA 15, Al 10	0.807	0.601
4.	Five-component system (general) NH_4ClO_4 75, $KClO_4$ 5, $(CH_3)_3NHNO_3$ 5, PMMA 5, Al 10	1.085	1.177

[a] CTPB–Carboxyl terminated polubutadiene.

Total oxidizing valences of the oxidizer

$= ((4 \times -1) + (1 \times 1) + (4 \times +2))$

$= 5.$

The magnitudes of the total reducing and oxidizing valences serve as numerical coefficients for the oxidizer and the fuels for stoichiometric balance. Assuming completely oxidized products, one can write the stoichiometrically balanced equation as

$$52\,NH_4ClO_4 + 5C_{10}H_8 + 5CH_3NH_3NO_3 \rightarrow 55CO_2 + 52HCl + 113H_2O + 31N_2.$$

The stoichiometric compositions of various three-component systems given later in the paper (Table 3) were calculated using this procedure. The treatment could be extended to the general case, where the two fuels are taken in different molar proportions. In such cases one has simply to multiply the reducing valences by the molarity of the fuel components and to get the appropriate total reducing valences. For example, when the fuels are taken in the ratio of 1:2, the system could be balanced as follows.

Total reducing valences of the fuels (0.5 $C_{10}H_8$ and 1.0 $CH_3NH_3NO_3$)

$= 0.5\,((10 \times -4) + (8 \times -1)) + ((1 \times -4) + (6 \times -1) + (3 \times 2))$

$= -28.$

Total oxidizing valences of the oxidizer

$= ((4 \times -1) + (1 \times 1) + (4 \times +2))$

$= 5.$

The balanced equation can be written as

$$28NH_4ClO_4 + 2.5\,C_{10}H_8 + 5\,CH_3NH_3NO_3 \rightarrow 30CO_2 + 28HCl + 67H_2O + 19N_2.$$

HEATS OF REACTION OF STOICHIOMETRIC MIXTURES

Clearly, all stoichiometrically balanced fuel-oxidizer mixtures result in a unique value of ϕ_e, that is,

$$\phi_e = \frac{p}{r} = 1 \quad \text{or} \quad p = r = P_0(\text{say}).$$

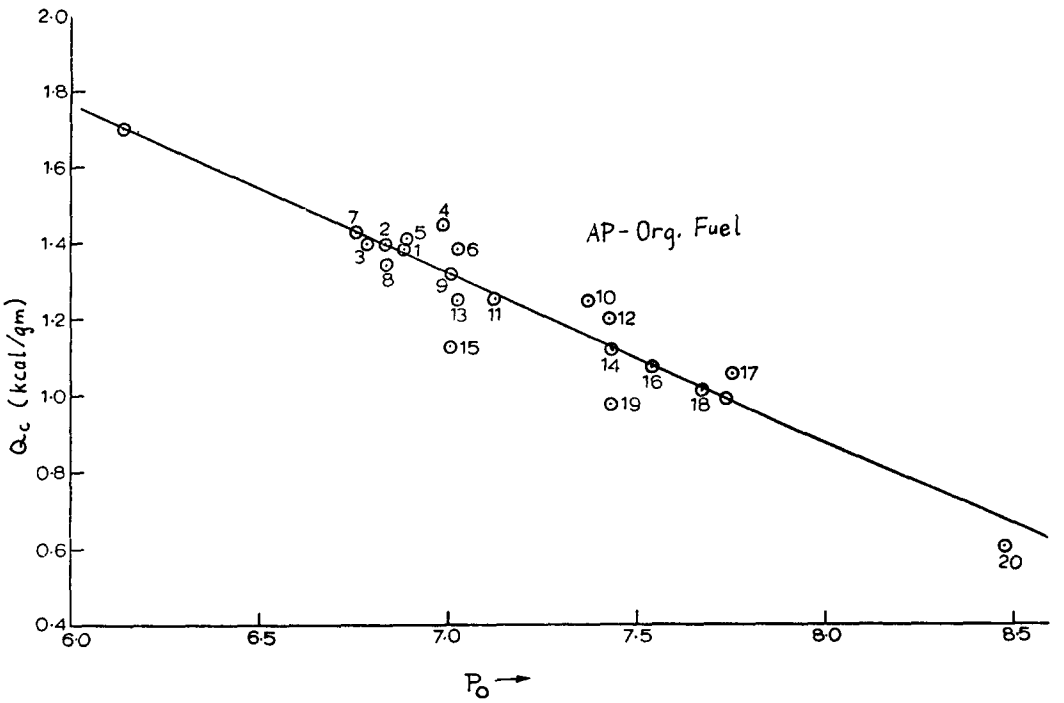

Fig. 1. Q_c-P_0 relation for NH_4ClO_4-organic fuels–1. naphthalene, 2. triphenylamine, 3. indole, 4. trimethylammonium nitrate, 5. diphenyl, 6. monomethyl ammonium nitrate, 7. azoxybenzene, 8. benzamide, 9. benzoic acid, 10. sucrose, 11. phthalic acid, 12. glucose, 13. alanine, 14. fumaric acid, 15. hydantoic acid, 16. citric acid, 17. glycollic acid, 18. malonic acid, 19. tartaric acid, 20. oxalic acid.

It is interesting to note, however, that the magnitude of the total composition of oxidizing or reducing elements (P_0), differs when various fuel-oxidizer mixtures are considered. For various mixtures having a common set of elements (C, H, N, Cl, and O), it is seen that P_0 shows a linear relationship with the heat of reaction Q_c of the mixture (Fig. 1) calculated, using the available thermochemical data [3-6].

To test the relationship rigorously, 20 fuels were chosen, and the linear plot was drawn using the least-square method. It is seen from the plot that P_0 bears a linear relationship with the heats of reaction of various AP-fuel mixtures at stoichiometric compositions. As the heat of reaction increases, the magnitude of P_0 decreases. The physical significance of such a relation originates from the following considerations.

P_0 essentially represents the total number of valences of a fixed mass of reactants. As P_0 increases the number of bonds increases which results in the lowering of the energetics of the reactants. In other words, the negative heats of the formation of the reactants increases. Since the heat of reaction is the difference in the proportionately summed up bond energies of the products and reactants, an increase in the P_0 value, therefore, should result, in the lowering of the net heat of reaction. The heat of reaction, Q_c (k cal/gm), of a mixture of any organic fuel and AP at stoichiometric composition can be obtained by the following equation, which is derived from the linear relationship of Q_c versus P_0, without involving their heats of formation or any other thermodynamic parameter.

$$Q_c = 4.395 - 0.439\,P_0. \quad (1)$$

For illustration, in Table 2, values of heat of reaction of some typical AP-fuel systems from Eq. (1)

TABLE 2

Heats of Reaction and P_0 Values of Various Systems at Stoichiometric Compositions

System No.	System[a]	P_0	Q_c (Kcal/gm) Calculated Using $Q_c - P_0$	Q_c (Kcal/gm) Calculated from Heats of Formation
1.	NH_4ClO_4–$C_{10}H_8$	6.879	1.378	1.393
2.	NH_4ClO_4–C_6H_5COOH	7.013	1.318	1.323
3.	NH_4ClO_4–$C_6H_4(COOH)_2$	7.112	1.275	1.255
4.	NH_4ClO_4–$(CH_3)_3NHNO_3$	6.988	1.330	1.459

[a] $C_{10}H_8$ = naphthalene, C_6H_5COOH = benzoic acid, $C_6H_4(COOH)_2$ = phthalic acid, $(CH_3)_3NHNO_3$ = trimethylammonium nitrate.

are compared with those calculated by the usual method using heats of formation data.

This work was extended to hydrazinium perchlorate ($N_2H_5ClO_4$)-organic fuel systems. Using the same set of fuels as in the case of AP, we see that hydrazinium perchlorate-fuel mixtures also show a linear relationship between P_0 and Q_c (Fig. 2). Surprisingly, the intercept and slope of the curve are virtually the same as observed in the case of AP-fuel systems.

This relationship was further extended to three-component systems having (1) one oxidizer, AP, and two organic fuels and (2) two oxidizers, AP and HP, and one fuel. At stoichiometric composi-

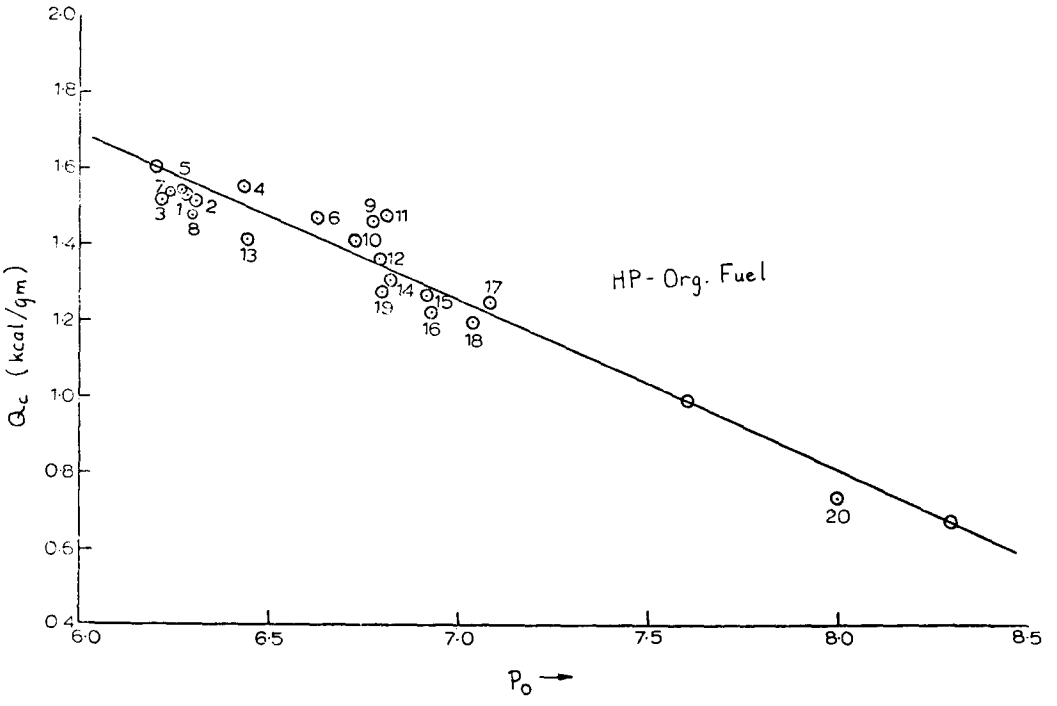

Fig. 2. Q_c–P_0 relation for $N_2H_5ClO_4$-organic fuels. (Numbers correspond to same fuels as in Fig. 1.)

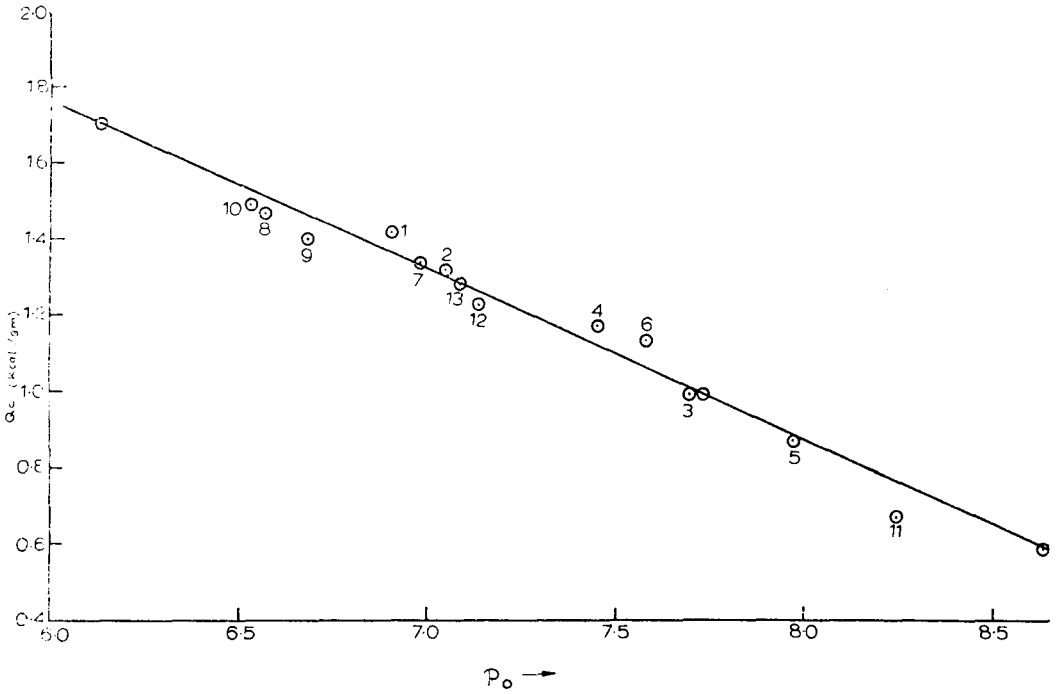

Fig. 3. Q_c-P_0 relation for three component systems. (Numbers correspond to various systems shown in Table 4.)

TABLE 3

Heats of Reaction and P_0 Values for Three Component Systems

System No.	System[a]	Composition Percentage by Weight			Q_c (K cals/gm)	P_0
1.	AP-$C_{10}H_8$-$CH_3NH_3NO_3$	85.75	7.30	6.95	1.420	6.910
2.	AP-$C_{10}H_8$-$C_2H_2O_4$	84.35	9.19	6.46	1.324	7.036
3.	AP-$C_4H_4O_4$-$C_2H_2O_4$	61.50	21.68	16.82	1.100	7.700
4.	AP-$C_6H_8O_7$-$C_6H_{12}O_6$	72.63	14.13	13.25	1.181	7.476
5.	AP-$C_4H_6O_6$-$C_2H_2O_4$	54.02	28.74	17.24	0.895	7.970
6.	AP-$C_6H_{12}O_6$-$C_2H_2O_4$	69.35	20.43	10.22	1.151	7.582
7.	AP-$C_6H_{12}O_6$-$C_{12}H_{10}$	85.23	7.96	6.81	1.356	6.982
8.	AP-HP-$C_{10}H_8$	42.88	48.36	8.76	1.468	6.569
9.	AP-HP-$C_7H_6O_6$	46.23	41.00	12.77	1.405	6.699
10.	AP-HP-$C_{18}H_{15}N$	48.12	42.67	9.20	1.475	6.538
11.	AP-HP-$C_2H_2O_4$	20.23	17.94	61.83	0.674	8.245
12.	AP-HP-$C_4H_4O_4$	39.32	34.87	25.82	1.221	7.123
13.	AP-HP-$C_6H_{12}O_6$	41.73	37.01	21.26	1.327	7.087

[a] $C_{10}H_8$ = naphthalene, $C_2H_2O_4$ = oxalic acid, $C_4H_4O_4$ = fumaric acid, $C_6H_8O_7$ = citric acid, $C_4H_6O_6$ = tartaric acid, $C_6H_{12}O_6$ = glucose, $C_7H_6O_2$ = benzoic acid, $C_{12}H_{10}$ = diphenyl, $C_{18}H_{15}N$ = triphenylamine, AP = ammonium perchlorate, HP = hydrazinium perchlorate.

tions, here again, Q_c varies linearly with P_0 (Fig. 3). These data are tabulated in Table 3.

In a solid propellant or an explosive composition, apart from an oxidizer and a binder (organic fuel), aluminium is added for achieving higher energetics. It is therefore interesting to see if the preceding correlation holds for three-component systems having aluminium as one of the ingredients. The Q_c values of various stoichiometric compositions having AP-Al-organic fuels, when plotted against P_0 (taking the valency of Al as −3), once again show a linear relationship (Fig. 4) having approximately the same slope and intercept as given by Eq. (1). This method, however, must be worked out first before actually applying it to other systems having oxidizers other than AP and HP, and other metallic ingredients.

EVALUATION OF p AND r

Although p and r values of given mixtures can be calculated by the previously mentioned method, they can be calculated easily using an analytical method. Figure 5 shows, for example, the variation of ϕ_e, p, and r with the % AP (C) in the composition of an AP-naphthalene mixture. It is seen that whereas ϕ_e versus C is a curve, p and r vary linearly with the composition and therefore can be calculated easily. From the nature of the curves it is clear that the two parameters can be represented by the following equations.

$$p = k_{0x} + m_{0x}\, C \tag{2}$$

and

$$r = k_{\text{red}} - m_{\text{red}}\, C, \tag{3}$$

where k is the intercept on the y-axis and m is the slope. C is the % AP in the composition. For hydrocarbon fuels, Eq. (2) reduces to

$$p = m_{0x}\, C.$$

From the graphical plot we get

$$p = 0.0766\, C$$

and

$$r = 37.50 - 0.341\, C.$$

At stoichiometric composition, $p = r$.

Therefore

$$C = 89.82.$$

Therefore, the mixture composition is AP, 89.82; naphthalene, 10.18.

The p and r parameters for a mixture of known composition, however, could be evaluated easily with the knowledge of the p and r values of their individual components and do not require plotting of the data.

The general relation is given in Eq. (2), where k_{ox} can be written as $k_{\text{ox}} = p$ at $C = 0$; that is, "p" value for 100 gm of fuel, alone, and

$$m_{0x} = \frac{(p)_{C=100} - (p)_{C=0}}{100}$$

where $(p)_{C=100}$ means "p" value of the oxidizer alone.

When $p_{\text{oxidizer}} > p_{\text{fuel}}$, the slope of the curve is $+ve$. The slope may be $-ve$, for example, in the case of AP-oxalic acid system (Table 4).

Similarly, r can be expressed as in Eq. (3), where $k_{\text{red}} = r$ at $C = 0$, that is, r value for 100 gm of fuel alone, and

$$m_{\text{red}} = \frac{(r)_{C=100} - (r)_{C=0}}{100}.$$

For AP-organic fuel systems, $(p)_{C=100} = 7.660$ and $(r)_{C=100} = 3.404$, "p," "r," values, and p – C, r – C relations for some typical AP-fuel systems are given in Table 4.

It is seen that the calculation of p and r at various compositions is extremely simple. The calculation of ϕ_e can therefore be performed equally easily since it is given by the ratio of p and r at various compositions. Furthermore, the stoichiometric compositions of a fuel-oxidizer mixture can easily be obtained.

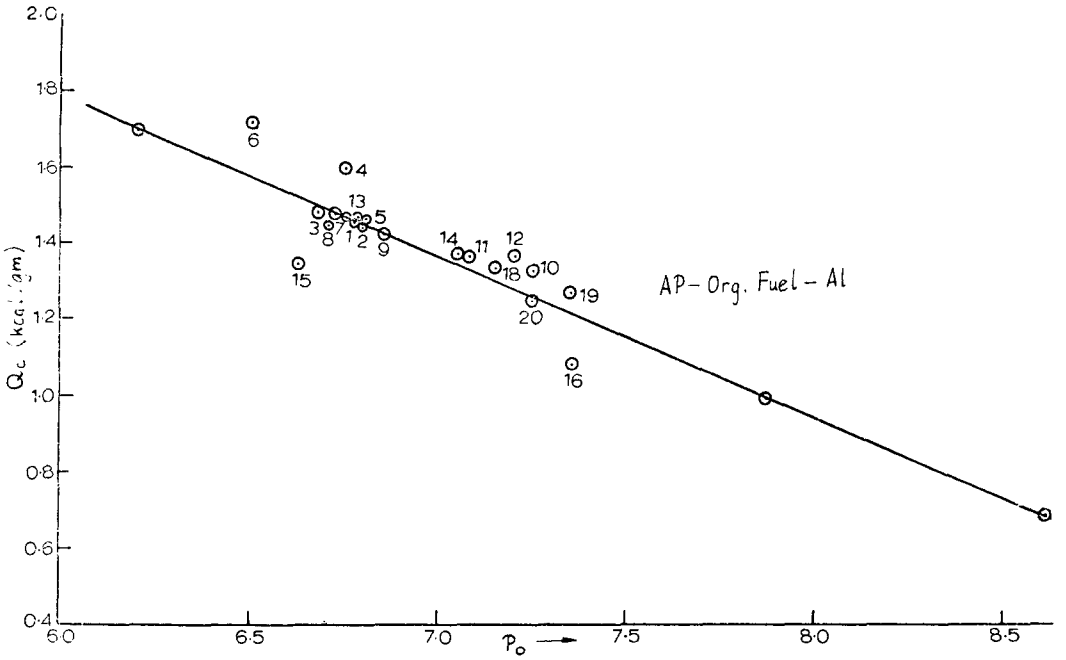

Fig. 4. Q_c-P_0 relation for NH_4ClO_4-organic fuel-A1. (The numbers correspond to the same set of fuels as in Fig. 1.)

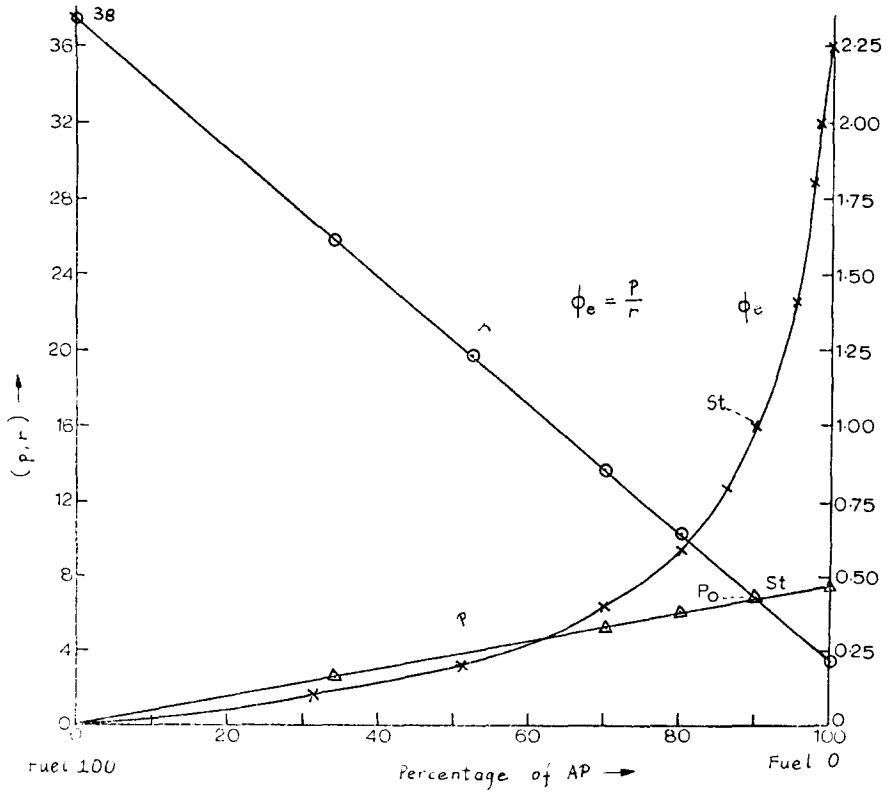

Fig. 5. Variation of ϕ_e, p, and r with concentration of AP for NH_4ClO_4-naphthalene system.

TABLE 4

Calculation of p and r from Composition of the Mixtures for AP, $(p)_{C=100} = 7.66$, $(r)_{C=100} = 3.404$

System	$(p)_{C=O}$ Fuel Alone	$(r)_{C=O}$ Fuel Alone	p-c Relation	r-c Relation
NH_4ClO_4-$C_{10}H_8$	0	37.50	$p = 0.0766C$	$r = 37.50-0.341C$
NH_4ClO_4-C_6H_5COOH	3.279	27.869	$p = 3.279+0.044C$	$r = 27.869-0.245C$
NH_4ClO_4-$C_6H_4(COOH)_2$	4.819	22.891	$p = 4.819+0.028C$	$r = 22.891-0.195C$
NH_4ClO_4-$(CH_3)_3NHNO_3$	4.918	28.033	$p = 4.918+0.027C$	$r = 18.033-0.146C$
NH_4ClO_4-$C_2H_2O_4$	8.888	11.110	$p = 8.888-0.1228C$	$r = 11.11-0.077C$

CONCLUSION

It is seen that the simple method proposed for evaluating elemental stoichiometric coefficient could easily be applied to multicomponent fuel-oxidizer systems. The total composition of oxidizing (or reducing) elements of the mixture appears to be related to the heats of reaction at a stoichiometric mixture ratio. The calculation of these parameters being very easy, they could be used for rapid calculation of ϕ_e at any given composition of the mixture.

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