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# Thermodynamic Charts for the Combustion Products of Nitric Acid and Kerosene

*By*

W. H. WILLIAMS, B.Sc.

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# Thermodynamic Charts for the Combustion Products of Nitric Acid and Kerosene

By

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COMMUNICATED BY THE PRINCIPAL DIRECTOR OF SCIENTIFIC RESEARCH (AIR),  
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*Summary.*—Thermodynamic charts giving enthalpy, entropy, temperature, pressure and specific volume, have been constructed for the products of combustion of a hydrocarbon fuel (85 per cent C, 15 per cent H by weight) with nitric acid (98 per cent by weight). The charts have been drawn for the following mixture ratios of the propellants:

- (a) stoichiometric proportion
- (b) 10 per cent by weight excess of fuel
- (c) 50 per cent by weight excess of fuel
- (d) 10 per cent by weight excess of oxidant

Graphs of combustion temperature and specific impulse against mixture ratio are also shown.

The procedure for calculating the initial enthalpy of the separate propellants (before combustion) and that of the propellant mixture is described.

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1. *Introduction.*—This note presents in four charts, Figs. 1 to 4, the thermodynamic properties of the combustion products of four mixtures of the propellants nitric acid (98 per cent) and kerosene. The charts have been drawn up for application to rocket motor conditions and extend over pressures from about 100 to 0.1 atmospheres. By means of the charts, graphs have been prepared of the theoretical combustion temperature against mixture ratio (Fig. 6) and of the theoretical specific impulse against mixture ratio (Fig. 7) for combustion pressures of 10, 20, 30 and 40 kg/cm<sup>2</sup>.

Although the c.g.s. system of units is preferred and has been used throughout this note, conversion to the f.p.s. system can be made by use of the table set out on the rider scale.

The term 'mole' refers to the molecular (or formula) weight in grams.

2. *Method.*—The calculations necessary for preparing the charts have been made by a numerical adaptation of the graphical method of Lutz<sup>1</sup>.

3. *Data.*—The chemical formula of the fuel (kerosene) is taken to be C<sub>17</sub>H<sub>36</sub> for calculation purposes. Values of the entropies of the products of combustion used in the calculations have been taken from Justi<sup>2</sup>. The enthalpies and equilibrium constants are those given by Lutz in the

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\* R.A.E. Tech. Note R.P.D. 33, received 29th January, 1954.

report mentioned above<sup>1</sup>. The standard reference state in this note is taken as 273·16 deg K (0 deg C) and 1 atmosphere (1 kg/cm<sup>2</sup>). At this reference state the enthalpies of C (graphite), H<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub> are taken arbitrarily as zero.

It should be noted that the 'atmosphere' used by Lutz is the 'technical atmosphere' which is equivalent to a pressure of 1 kg/cm<sup>2</sup> and is related to the standard physical atmosphere as indicated by the following expression:

$$1 \text{ physical atmosphere (At)} = 1\cdot033227 \text{ kg/cm}^2 = 1\cdot033227 \text{ technical atmospheres(at)}$$

$$\text{or } \frac{1 \text{ physical atmosphere}}{1 \text{ technical atmosphere}} = 1\cdot033227$$

The constant pressure lines on the charts have been shown in units of kg/cm<sup>2</sup>.

Since performing the calculations from which the charts were constructed values<sup>3</sup> more reliable than those of Justi<sup>2</sup> for the absolute entropies of the gaseous products of combustion have become available, together with data on monatomic nitrogen. In addition Lutz<sup>3</sup> has recently published more up-to-date tables of thermodynamic properties together with constants for combustion equilibrium reactions to replace those given in his original report<sup>1</sup>; the new data are based on the new standard reference state of 298·16 deg K and 1 kg/cm<sup>2</sup> pressure.

4. *Assumptions.*—It is necessary to make certain assumptions concerning the nature of the product gases and the changes they undergo during expansion.

In the first place it is assumed that each separate component of the product mixture will behave 'ideally', that is, in accordance with the general gas law.

$$pv = \frac{R}{M} T$$

where

$p$  is pressure

$v$  is specific volume

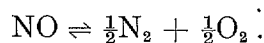
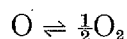
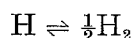
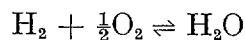
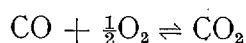
$R$  is the universal gas constant

$M$  is molecular weight

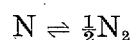
and  $T$  is absolute temperature.

It is assumed that the various gases in the product mixture are in equilibrium in all conditions. This assumption is probably more reasonable than that of a 'frozen' equilibrium, *i.e.*, an equilibrium in which the initial composition of the combustion products remains unaltered during expansion. The assumption made, therefore, is that there is always sufficient time to attain complete equilibrium even in the later stages of expansion when the gas velocity is large.

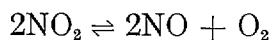
Dissociation of the products of combustion becomes an important factor at temperatures above about 2,000 deg K, and particularly at low pressures; it has, therefore, received full consideration in the calculations. The dissociation reactions considered are:



The dissociation reaction



is neglected in the calculations because the proportion of monatomic nitrogen existing under these conditions is negligible; furthermore the data on the enthalpy and equilibrium constant for this reaction were not readily available when the calculations were made. The combustion product nitrogen dioxide  $\text{NO}_2$  has also been ignored.  $\text{NO}_2$  begins to dissociate at around 200 deg C according to the reaction.



and dissociation is completed at about 650 deg C  $\approx$  900 deg K. This temperature would probably only be encountered in the extreme case of a 50 per cent fuel rich mixture (Fig. 3) and even then only for an expansion from 100 kg/cm<sup>2</sup> to 0.1 kg/cm<sup>2</sup>.

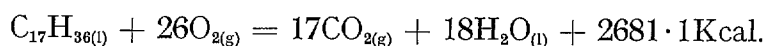
The assumption that the processes are adiabatic implies, of course, that there are no losses due to shock waves, friction and heat transfer during expansion. Every process is, therefore, reversible and the expansion is isentropic.

5. *Initial Enthalpy of the Propellant Mixture.*—The initial enthalpy of the hydrocarbon fuel (85 per cent C, 15 per cent H) is determined from knowledge of its heat of combustion (or calorific value). The heat of combustion gives the quantity of heat available when the fuel is fully burnt to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  and the resulting gases are cooled down to the original conditions of temperature and pressure; these conditions are taken here to be 25 deg C (298.16 deg K) and 1 kg/cm<sup>2</sup>. The 'higher' or 'lower' value of the heat of combustion is used depending on whether  $\text{H}_2\text{O}$  in the cooled products is taken to be in the state of liquid or gas.

A value of the higher heat of combustion provided by the R.P.D. chemical laboratory of 20,070 B.Th.U/lb or 2681.1 Kcal/mole is taken as a representative figure in all the charts for a typical hydrocarbon fuel (aviation kerosene with the approximate composition 85 per cent C 15 per cent H by weight). Since the heat of combustion for a sample of fuel may vary appreciably with different supplies, it is recommended that a separate determination of the value be made before using the charts and accepting the initial enthalpy levels.

The determination of the initial enthalpy will now be considered; the state is denoted by a suffix <sub>(g)</sub> for gas and <sub>(l)</sub> for liquid.

5.1. *Fuel.*—The complete combustion of 1 mole of fuel in gaseous oxygen is represented by the equation



This may be written in energy form thus:

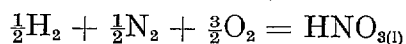
$$I_{\text{C}_{17}\text{H}_{36(l)}}^{25^\circ\text{C}} + 26I_{\text{O}_{2(g)}}^{25^\circ\text{C}} = 17I_{\text{CO}_{2(g)}}^{25^\circ\text{C}} + 18I_{\text{H}_2\text{O}_{(l)}}^{25^\circ\text{C}} + 2681.1\text{Kcal}$$

where  $I^{25^\circ\text{C}}$  denotes enthalpy in Kcal/mole at 25 deg C as given by Lutz<sup>1</sup>.

Therefore  $I_{\text{C}_{17}\text{H}_{36(l)}}^{25^\circ\text{C}} + 26(0) = 17(-94.052) + 18(-68.318) + 2681.1\text{Kcal}$ ,

*i.e.*,  $I_{\text{Fuel}}^{25^\circ\text{C}} = -147.5\text{Kcal/mole}$  of fuel; and this defines the initial enthalpy of the fuel in accordance with the definition of enthalpy as given by Lutz<sup>1</sup>.

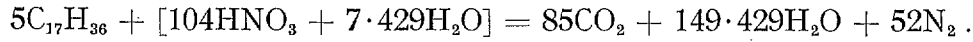
5.2. *Oxidant.*—Bichowsky and Rossini<sup>5</sup> give  $-41.660\text{Kcal/mole}$  as the enthalpy of liquid nitric acid at 18 deg C. Now as



by changing the temperature for both sides of this equation from 18 deg C to 25 deg C, using Kelley's heat capacity equations<sup>6</sup> for the gaseous elements on the left-hand side, and taking 0.029 Kcal/mole for the heat capacity of  $\text{HNO}_{3(l)}$  we obtain the value  $-41.570\text{Kcal/mole}$  for the enthalpy of liquid nitric acid at 25 deg C. Hence

$$I_{\text{HNO}_{3(l)}}^{25^\circ\text{C}} = -41.570\text{Kcal/mole.}$$

5.3. *Propellant—Stoichiometric Ratio.*—Considering now the complete reaction of the fuel with nitric acid of 98 per cent concentration, we have



The reactants on the left hand side of the equation are taken to be liquids at a temperature of 25 deg C (this is chosen as the room or laboratory temperature since most up-to-date thermal data are quoted for  $T = 298 \cdot 16$  deg K). To determine the initial enthalpy of the mixture of fuel and oxidant we need consider only the left-hand side of the equation, and, therefore,

$$i_{\text{mixture}}^{25^\circ\text{C}} = 5(-147 \cdot 5) + 104(-41 \cdot 570) + 7 \cdot 429(-68 \cdot 318) \text{ Kcal}$$

or 
$$i = -\frac{5 \cdot 147 \cdot 5 - 104 \times 41 \cdot 570 - 7 \cdot 429 \times 68 \cdot 318}{7 \cdot 886} \text{ Kcal/kg of mixture.}$$

Therefore 
$$i = -706 \text{ Kcal/kg of mixture}$$

where  $i$  denotes the enthalpy in Kcal/kg.

5.4. *Propellant—Any Mixture Ratio.*—Generally, if the propellant mixture consists of oxidant and fuel in the ratio  $R$  to 1 by weight, then the initial enthalpy in Kcal/kg of mixture is given by

$$i_{\text{mixture}}^{25^\circ\text{C}} = \left[ \frac{1}{R+1} \frac{I_F^{25^\circ\text{C}}}{M_F} + \frac{R}{R+1} \frac{I_{\text{ox}}^{25^\circ\text{C}}}{M_{\text{ox}}} \right] \times 1000$$

where  $I_F^{25^\circ\text{C}}$  and  $I_{\text{ox}}^{25^\circ\text{C}}$  are the enthalpies at 25 deg C in Kcal/mole of fuel and oxidant respectively, and  $M_F$  and  $M_{\text{ox}}$  are the molecular weights in grams of fuel and oxidant respectively.

The initial enthalpy of the propellant mixture at any other temperature  $t$  deg C is obtainable from a knowledge of the heat capacities of the reactants.

Thus 
$$I_F^{t^\circ\text{C}} = I_F^{25^\circ\text{C}} + (t - 25)\overline{Cp}$$

where  $\overline{Cp}$  = mean heat capacity of fuel in Kcal/mole deg C over the temperature range  $t$  deg C to 25 deg C.

A similar calculation yields  $I_{\text{ox}}^{t^\circ\text{C}}$  whence  $I_{\text{mixture}}^{t^\circ\text{C}}$  can be obtained.

The values of the heat capacities of the reactants under consideration are given below:—

Reactant.. .. .	$C_{17}H_{36(l)}$	$HNO_{3(l)}$	$H_2O_{(l)}$
$\overline{Cp}$ (Kcal/mole deg C) ..	0.113	0.029	0.018

6. *Parameter  $\Gamma$ .*—The parameter  $\Gamma$  which appears in Figs. 6 and 7 is defined as

$$\Gamma = \frac{n_O}{n_O + 2n_C + \frac{1}{2}n_H}$$

where  $n_O$ ,  $n_C$ ,  $n_H$  represent the number of atoms of oxygen, carbon and hydrogen in the chemical representation of the mixture of propellants. The limiting values of  $\Gamma$  are clearly 0 for fuel only, and 1 for oxygen only; for the stoichiometric proportion of any C.H.O.N. propellant system  $\Gamma$  becomes 0.5.

If  $R$  is the mixture ratio by weight of 98 per cent nitric acid to kerosene then the relation between  $R$  and  $r$  is given by

$$R = \frac{r}{0.220875 - 0.26197r}$$

or

$$r = \frac{R}{4.52745 + 1.18606R}$$

7. *Charts.*—A rocket motor develops thrust by the expansion and consequent acceleration of the combustion products through a nozzle. For theoretical purposes the expansion is considered to be adiabatic. As it is necessary to calculate the dimensions of the nozzle as well as the gas properties, the charts are presented in the form of enthalpy—specific volume or  $i-v$  charts to facilitate these calculations.

The method of using the charts with the aid of the rider scale (Fig. 5), and the advantages this method has over the use of the well known Mollier diagram employed in steam engineering are illustrated by Spalding and Green<sup>7</sup>. The accompanying charts are simpler to use, however, than those described by Spalding and Green because the specific volume is plotted on a logarithmic scale. It should be noted that the logarithmic scale for the nozzle area marked at the top of the  $i-v$  charts refers to specific area, *i.e.*, the cross-sectional area of nozzle in sq cm corresponding to a flow rate of 1 kg/sec of propellant.

The initial enthalpy of the gaseous product mixture is denoted by a constant initial enthalpy line drawn on the chart and is equal to the initial enthalpy of the reactants, kerosene and 98 per cent nitric acid, both of which are taken to be liquid at 25 deg C. For any other precombustion temperature of the reactants as explained in section 5.4 a similar line can be drawn and along its length the theoretical combustion conditions of pressure, specific volume, entropy and flame temperature obtain. Isentropic expansion from a specific initial pressure of combustion to any other pressure can be followed on the  $i-v$  chart along a line of constant entropy starting from the initial enthalpy line at a point corresponding to the initial or combustion pressure.

If it is desired to carry out the expansion through a nozzle, then the nozzle dimensions can be very simply obtained with the aid of Fig. 5. Thus, if expansion is to take place from a pressure of 20 kg/cm<sup>2</sup> to an ambient pressure of 1 kg/cm<sup>2</sup> then the rider scale Fig. 5 is superimposed on the  $i-v$  chart so that the horizontal line on the rider scale coincides with the initial enthalpy line. The rider scale is now moved parallel to the  $v$ -axis of the chart until the velocity curve of the rider scale is tangential to the appropriate isentropic line for 20 kg/cm<sup>2</sup>. The arrow of the rider scale then indicates the specific throat area on the upper scale of the chart. If now the rider scale is moved to the right until the velocity curve, the isentrope for 20 kg/cm<sup>2</sup> and the constant pressure line  $p = 1$  intersect at a common point, the arrow indicates the specific exit area of the nozzle. The exhaust velocity in m/sec is now shown on the graduated velocity curve of the rider scale at the common point of intersection.

The specific impulse is then given by the expression:

$$\text{S.I.} = \frac{\text{velocity}}{g} = \frac{\text{velocity (m/sec)}}{9.80665 \text{ (m/sec}^2\text{)}} = \text{S.I. sec}$$

or alternatively

$$\text{S.I.} = 9.328 \sqrt{\Delta i} \text{ sec}$$

where  $\Delta i$  is the heat drop in Kcal/kg.

When the nozzle dimensions are known the gas conditions can be determined at any station along the axis of the nozzle. The mass flow rate can be calculated from the expression

$$Q = A/a \text{ kg/sec}$$

where  $a$  is the specific area of cross section at a station ( $\text{cm}^2/\text{kg/sec}$ )

$A$  area of cross-section at the same station ( $\text{cm}^2$ )

and  $Q$  propellant mass flow rate ( $\text{kg/sec}$ )

The graphs of combustion temperature and specific impulse against mixture ratio (Figs. 6 and 7) have been prepared from the  $i-v$  charts. They show, unfortunately, a degree of inconsistency which has arisen from the fact that the four  $i-v$  charts were prepared over a period of time and were not fully co-ordinated with one another. The error in specific impulse is of the order of  $\pm 2$  per cent at lower pressures and becomes negligible for expansion from 40 atmospheres.

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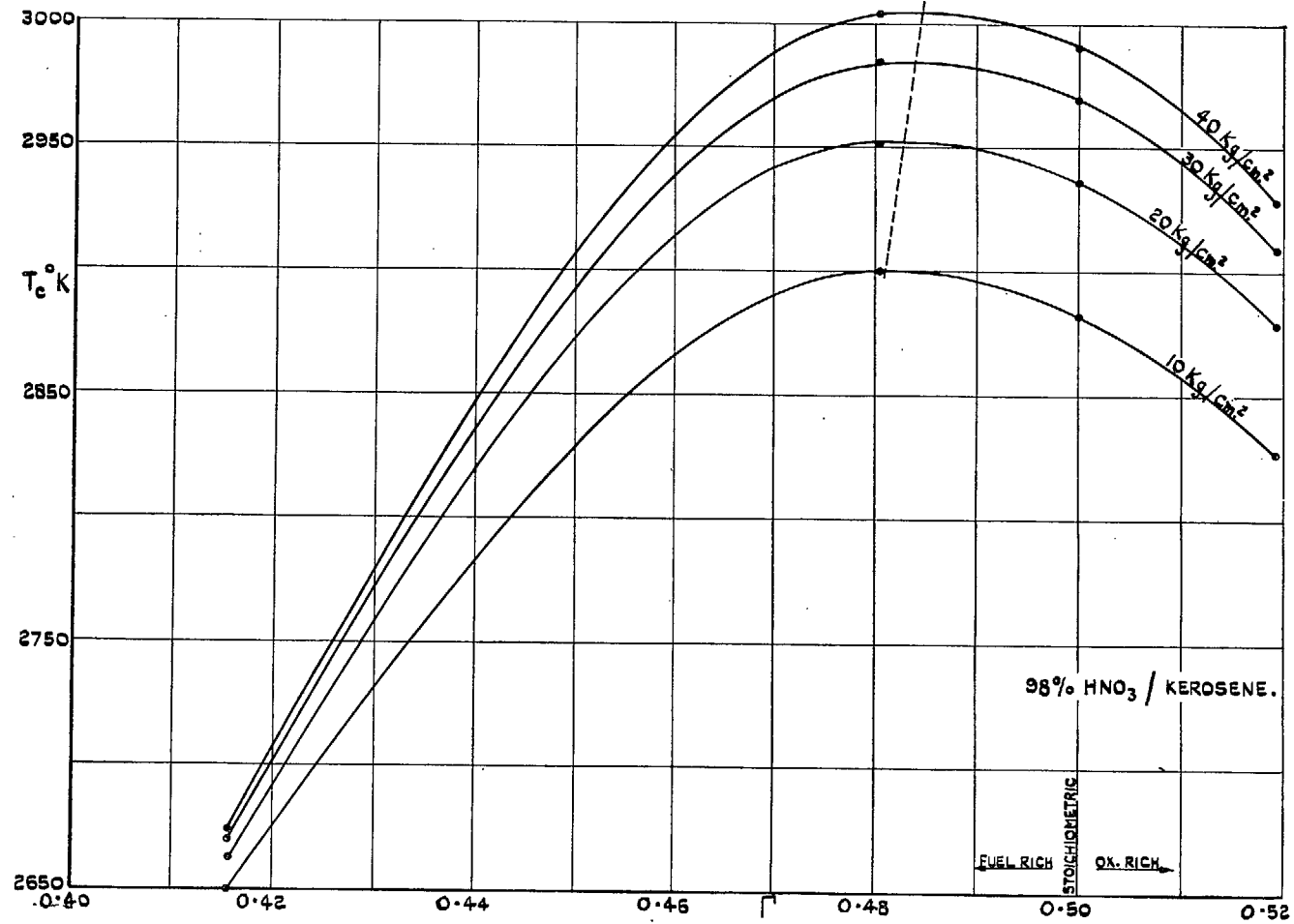


FIG. 6. Theoretical combustion temperature against mixture ratio.



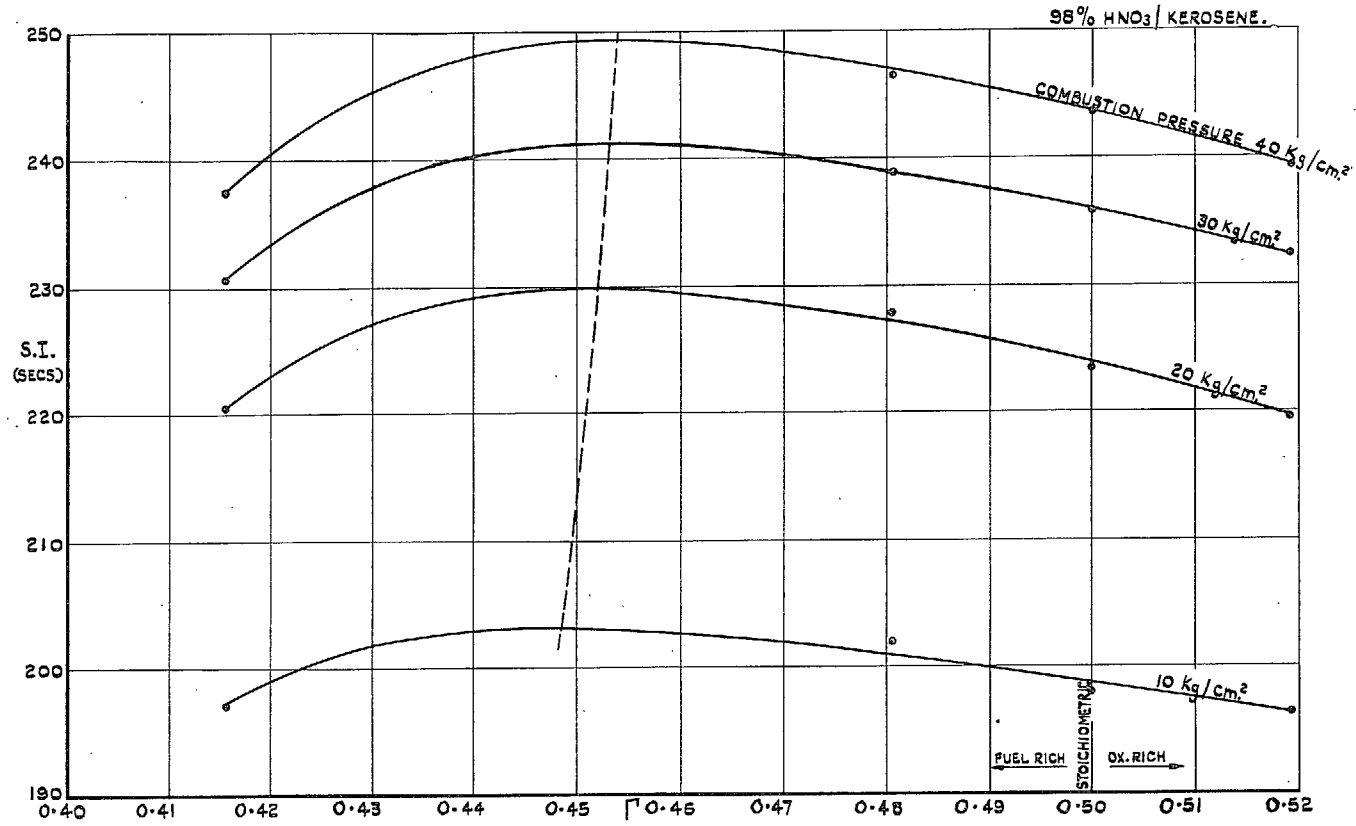


FIG. 7. Theoretical specific impulse against mixture ratio.

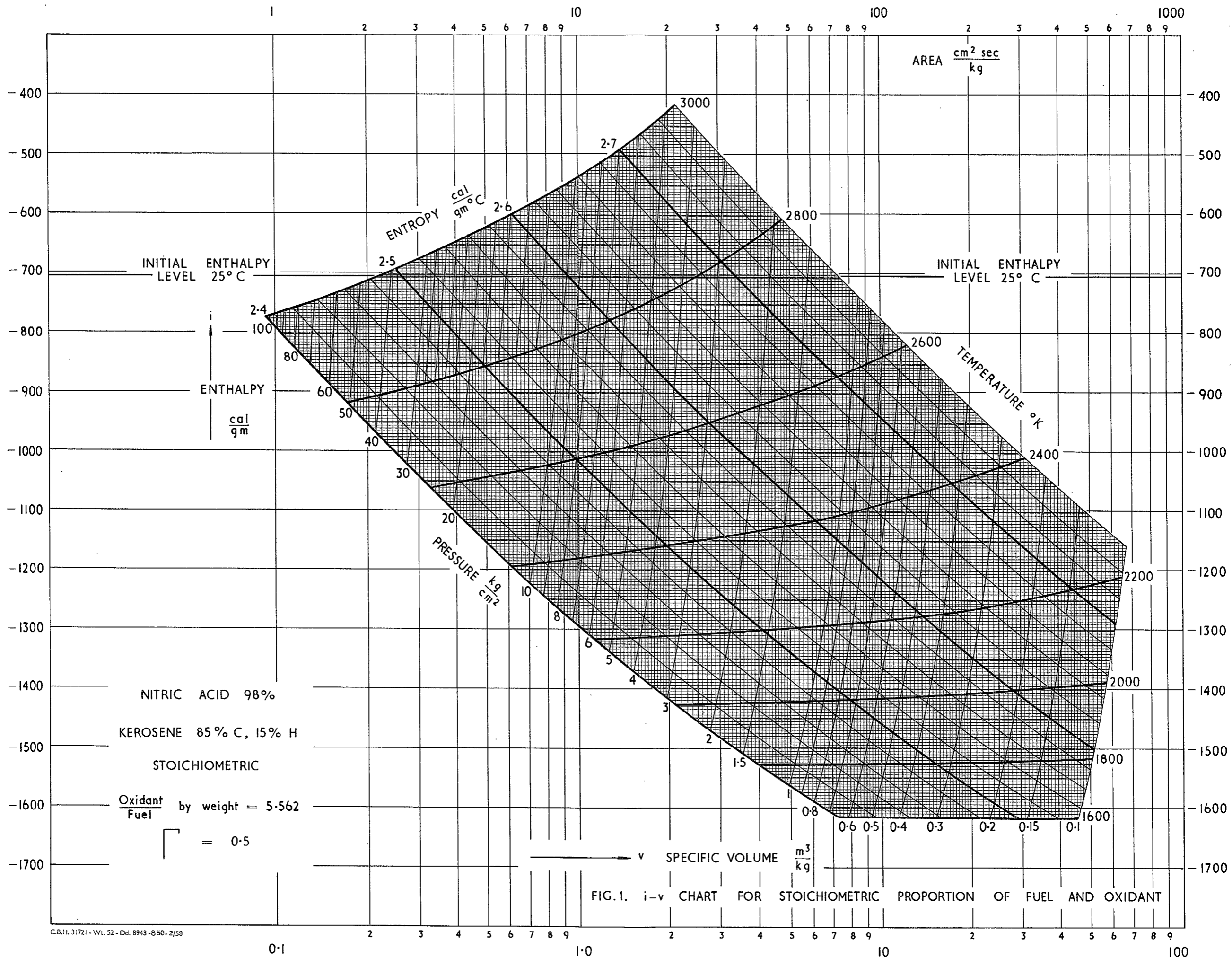


FIG. 1.  $i-v$  CHART FOR STOICHIOMETRIC PROPORTION OF FUEL AND OXIDANT

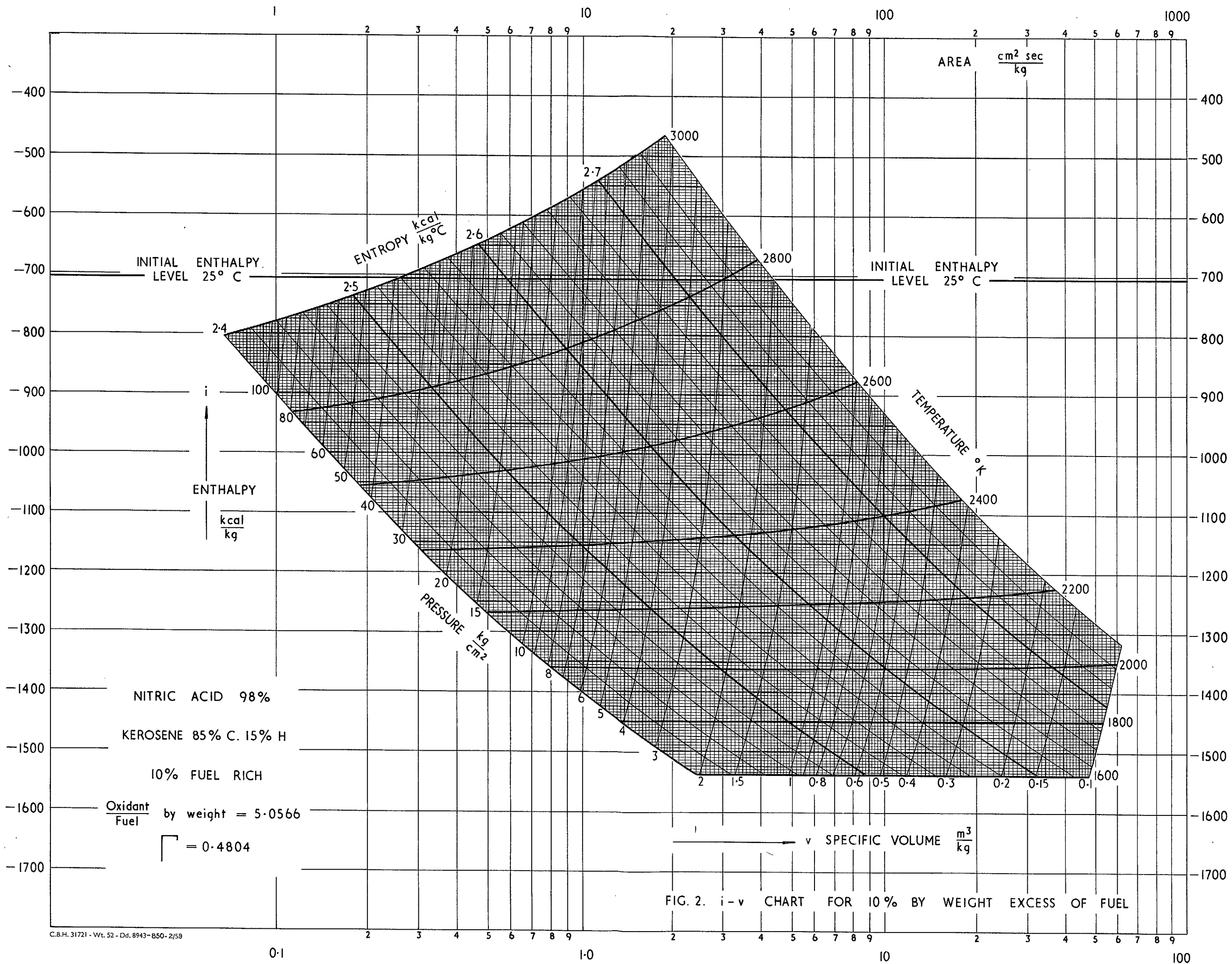


FIG. 2. i-v CHART FOR 10% BY WEIGHT EXCESS OF FUEL

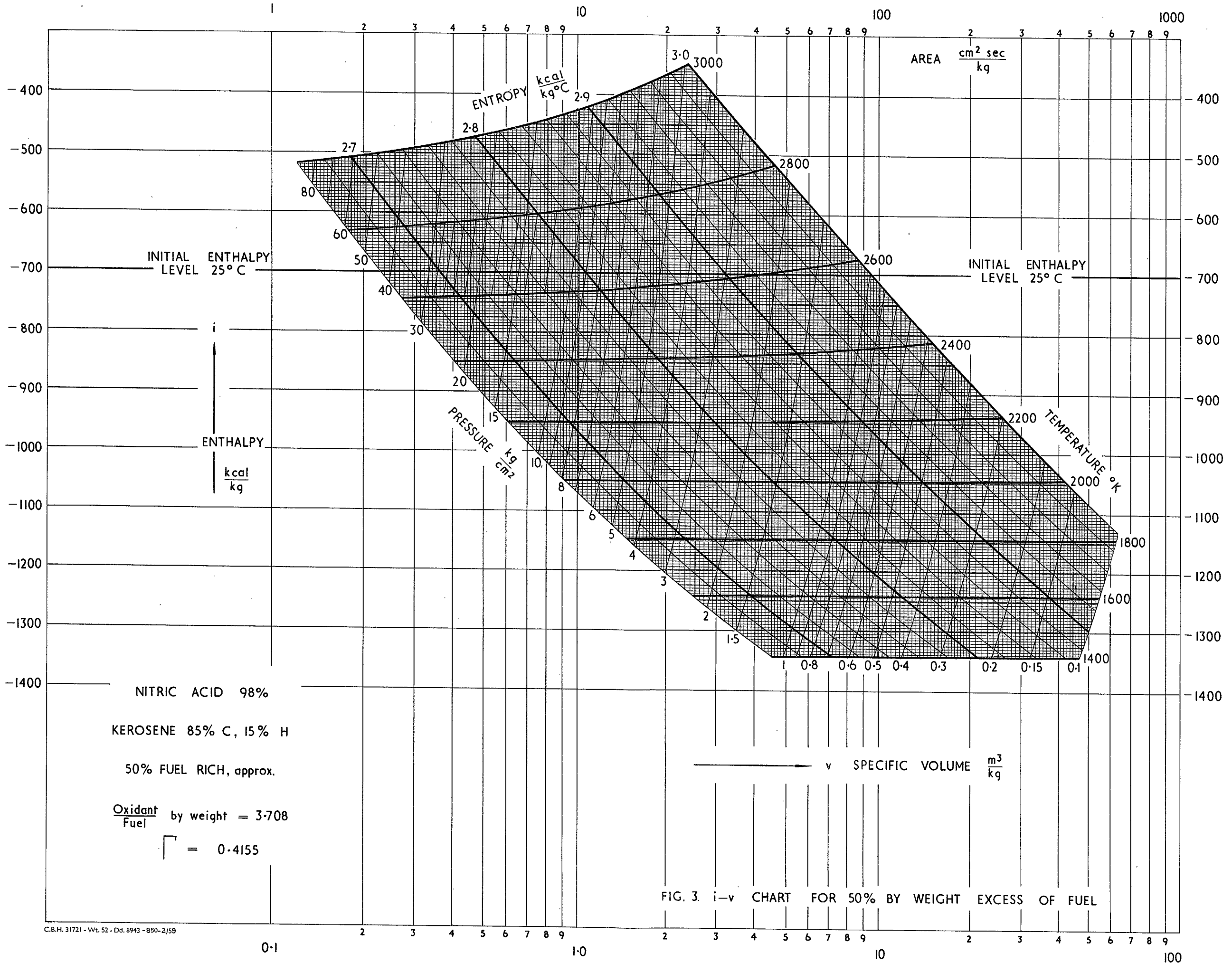


FIG. 3. i-v CHART FOR 50% BY WEIGHT EXCESS OF FUEL

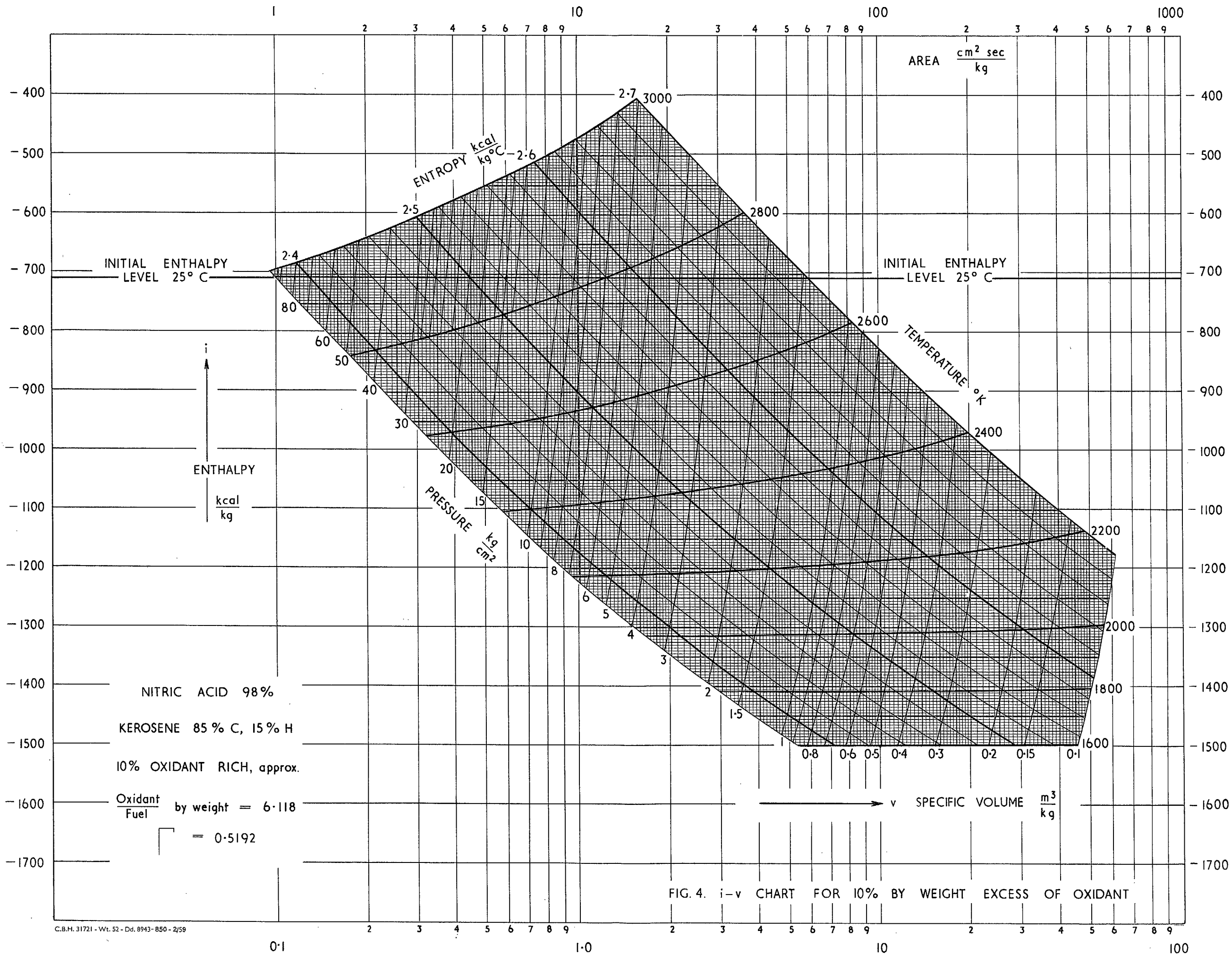


FIG. 4. i-v CHART FOR 10% BY WEIGHT EXCESS OF OXIDANT

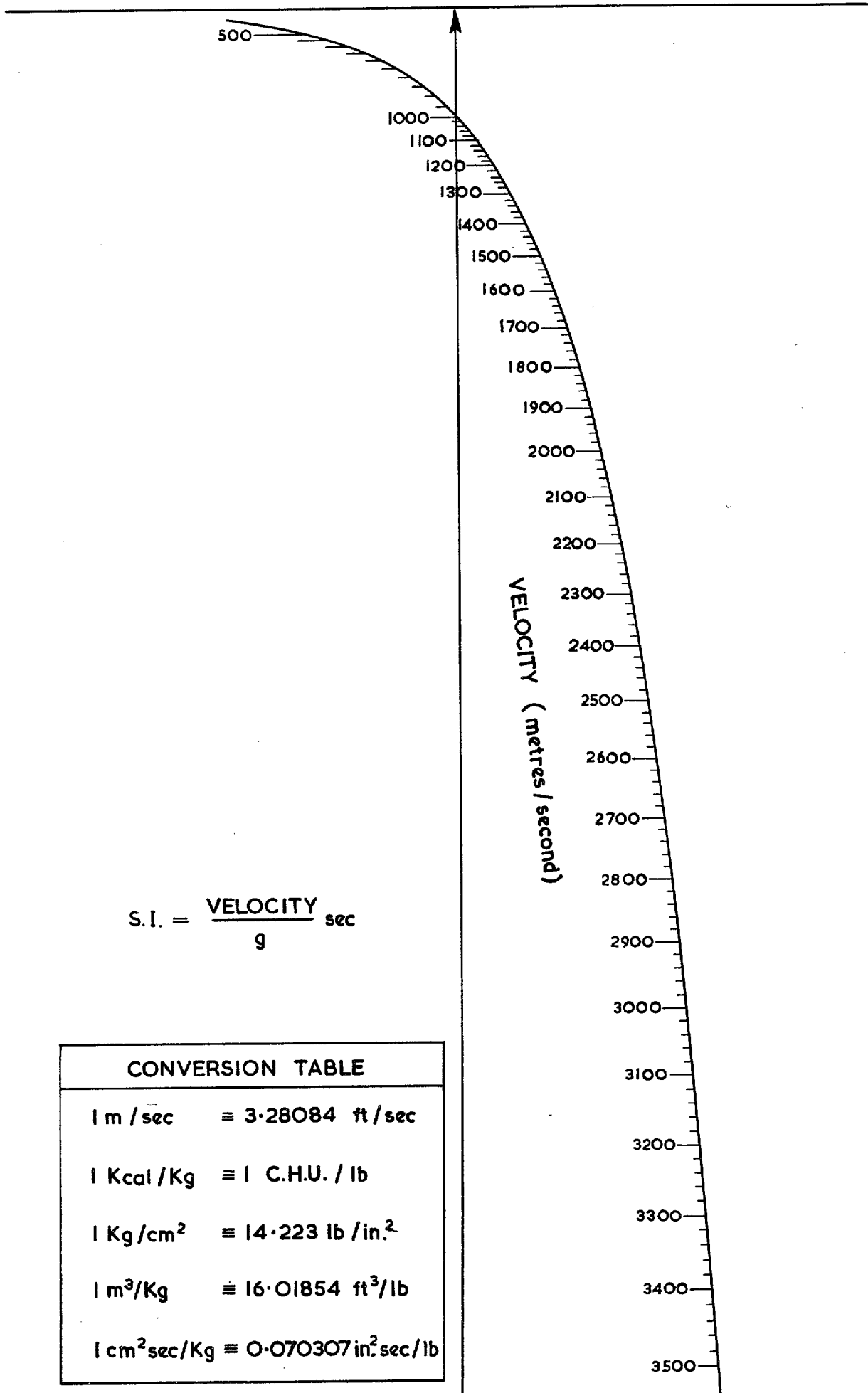


FIG.5. RIDER SCALE

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