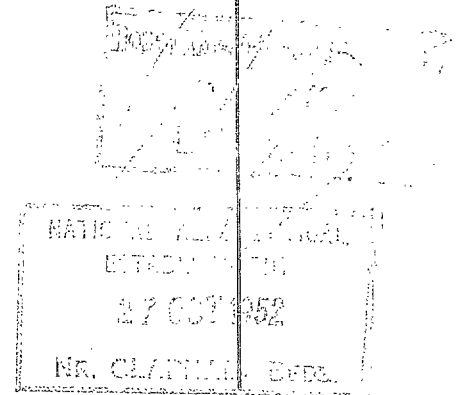


MINISTRY OF SUPPLY  
AERONAUTICAL RESEARCH COUNCIL  
REPORTS AND MEMORANDA



PART I

Tabulated Thermal Data for Hydrocarbon  
Oxidation Products at High Temperatures

PART II

The Effect of Dissociation on Rocket  
Performance Calculations

By

F/LT. A. B. P. BEETON

*Crown Copyright Reserved*

LONDON: HER MAJESTY'S STATIONERY OFFICE

1952

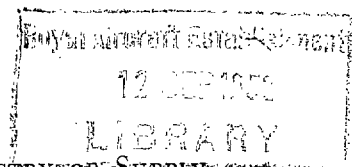
FOUR SHILLINGS NET

PART I

# Tabulated Thermal Data for Hydrocarbon Oxidation Products at High Temperatures

By

F/Lt. A. B. P. BEETON



COMMUNICATED BY THE PRINCIPAL DIRECTOR OF SCIENTIFIC RESEARCH (AIR), MINISTRY OF SUPPLY

---

*Reports and Memoranda No. 2542\**

*October, 1946*

---

*Summary.*—Tables are given of the total heat and entropy of  $H_2O$ ,  $CO_2$ ,  $O_2$ ,  $CO$ ,  $H_2$ ,  $OH$ ,  $O$  and  $H$  for the range of temperature 1500–4000 °K. Values are also given for the corresponding equilibrium constants over the same temperature range. The tables have been compiled with a view to their use in calculating the performance of liquid-fuel rockets.

1. *Introduction.*—1.1. In order to calculate the theoretical gas conditions in a rocket motor, it is necessary to have thermal data relating to all the combustion products at the high temperatures of operation. If it is assumed that all the components behave as perfect gases (*i.e.* obey the law  $PV = \frac{2776}{M} T$ ), then the theoretical performance may be exactly calculated from a knowledge of the various equilibrium constants and of the total heats and entropies of the components as functions of temperature over the operating range, which can be taken as between 1500 and 4000 °K.

1.2. Rough curves have already been given<sup>1</sup> for the quantities necessary in an approximate calculation. These values are given here in tabulated form, together with values for the additional components  $OH$ ,  $O$  and  $H$ .

1.3. The basic statistical data have for the most part already been worked out as values for one or other of the usual thermal quantities at various temperatures. The main work has been to examine very carefully all the available literature in order to obtain the latest and most accurate values, to convert them into the thermal quantities required, interpolating and extrapolating where necessary, and finally to check the completed tables for arithmetical errors by examination of differences. The values were also checked for thermodynamic consistency by the equations (5) and (6) given later in section 3.

2. *Sources of Data.*—2.1. Determination of the thermal properties of the simpler gases at high temperatures is most accurately done by statistical analysis of spectroscopic observations. This was first undertaken in America in the years 1930 to 1935. There do not appear to be any more recent major revisions of these calculations, which have accordingly been used in compiling the present tables.

---

\* R.A.E. Technical Notes Nos. Aero. 1835, 1838, received 23rd January, 1947, and 12th December, 1946.

2.2. Refs. 2 to 10 give the original papers. A book by Justi<sup>11</sup> contains some tables based on these values, but they are not presented in the most convenient form for the present purpose. Ref. 12 contains a more recent summary, with a few systematic alterations. It does not, however, cover all the components required in the present investigation.

2.3. The complex energy levels of the polyatomic CO<sub>2</sub> and H<sub>2</sub>O molecules have not yet been completely elucidated, and the order of accuracy of the data given for these gases is considerably less than is possible for the simpler molecules, especially at higher temperatures. However, it is not likely that the extrapolated values given here can be seriously in error.

2.4. In addition to these properties of the gases themselves, we require reliable values of the heats of reaction between the gases. The heats of reaction involving only those gases which remain undissociated at room temperature have recently been determined with considerable accuracy by the American Bureau of Standards<sup>12</sup>. The heats of reaction involving OH, O and H are not known with the same degree of accuracy, but the values taken here<sup>13</sup> are considered to be the most recent and most accurate ones available.

2.5. As a simplification involving trifling loss of accuracy, the present tables have been evaluated by the use of integral molecular weights (*i.e.* hydrogen = 2, etc.).

3. *Presentation of Results.*—3.1. The quantities presented in Tables 1 and 2 are respectively the 'absolute total heat'  $I'$  in C.H.U./lb of each component, and the absolute entropy  $\phi$  at 1 atm in C.H.U./lb °C.

3.2. For the purposes of calculating  $I'$ , the datum substances are taken as H<sub>2</sub>O, CO<sub>2</sub> and O<sub>2</sub> in their ideal states at 0 °K. This avoids all negative values.  $I'$  is independent of the pressure, and is expressed as follows as a function of the absolute temperature  $T$ .

$$I' = \int_0^T C_p^{\circ} \cdot dT + \Delta E_0, \quad \dots \quad (1)$$

where  $\Delta E_0$  is the heat of reaction to one or more of the datum substances at 0 °K. In an adiabatic process involving change of chemical composition, the work available is therefore equal to the decrease in the quantity  $\Sigma m I'$  C.H.U./lb, where  $m$  is the proportion by weight and  $I'$  the absolute total heat for each component of the mixture.

3.31. The entropy datum is also taken as 0°K and 1 atm abs, so that

$$\phi = \int_0^T \frac{C_p}{T} \cdot dT. \quad \dots \quad (2)$$

The entropy at pressure  $P$  atm is then given by

$$\phi - \frac{1.986}{M} \cdot \log_e P,$$

where  $M$  is the molecular weight of the component considered. Consequently the entropy of a mixture of components at their respective partial pressures  $P'$  (atm) is given by

$$\Phi = \Sigma m\phi - 1.986 \frac{\Sigma P' \log_e P'}{\Sigma M P'}, \quad \dots \quad (3)$$

where  $m$  is again the proportion by weight, which may also be expressed by

$$m = \frac{M P'}{\Sigma M P'}. \quad \dots \quad (4)$$

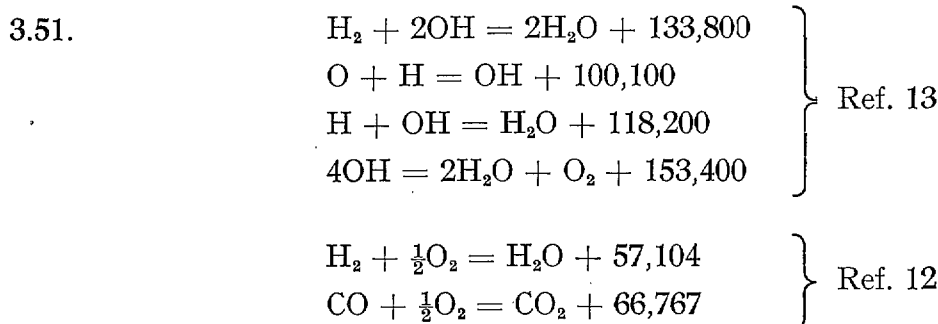
3.32. If the entropy of the mixture of gases is calculated on this basis, then the second and third laws of thermodynamics may be used to show that the value of this quantity remains unaltered in a reversible adiabatic expansion involving change of chemical composition.

3.33. In accordance with the usual convention, the contribution to the entropy provided by 'nuclear spin' has been subtracted from the absolute values in the case of H<sub>2</sub> and H. This is necessary because the equivalent contributions in the case of all the other gases occur well below the lowest experimentally obtainable temperature, and are therefore left out of the statistical analysis in order to make it agree with experiment. But with H<sub>2</sub> and H, it appears that the nuclear spin energy is released within the range of experimental temperatures, and that in these two special cases the absolute entropy is measured. A fuller explanation may be found in Ref. 8.

3.4. It will be noted that  $I'$  and  $\phi$  are not entirely independent, but are related by the equation

$$\frac{dI'}{dT} = T \cdot \frac{d\phi}{dT} \quad \dots \quad \dots \quad \dots \quad \dots \quad (5)$$

3.5. In determining the values of  $\Delta E_0$  to be added to the total heats obtained from spectroscopic data, the following heats of reaction at absolute zero are taken, expressed here as C.H.U./lb mol wt :



3.52. The following values of  $\Delta E_0$  (C.H.U./lb) are obtained from these equations,

$\frac{H_2O}{0}$	$\frac{CO_2}{0}$	$\frac{O_2}{0}$	2384	$\frac{H_2}{28,550}$	$\frac{OH}{2255}$	$\frac{O}{3662}$	$\frac{H}{79,850}$
------------------	------------------	-----------------	------	----------------------	-------------------	------------------	--------------------

3.6. Equilibrium constants are taken as below.

3.61.

$$K_1 = \frac{[CO] [O_2]^{1/2}}{[CO_2]}$$

$$K_2 = \frac{[H_2] [O_2]^{1/2}}{[H_2O]}$$

$$K_3 = \frac{[OH] [H_2]^{1/2}}{[H_2O]}$$

$$K_4 = \frac{[H]}{[H_2]^{1/2}}$$

$$K_5 = \frac{[O]}{[O_2]^{1/2}}$$

where [CO], [O<sub>2</sub>], etc. refer to the partial pressures of the various components expressed in atmospheres absolute.  $K_1, K_2, K_3, K_4$  and  $K_5$  are then functions of temperature only.

3.62. The equilibrium constants may be simply related to the other thermal properties as follows :

$$\Sigma M \left( \phi - \frac{I'}{T} \right) = 4.573 \log_{10} K \quad \dots \quad \dots \quad \dots \quad (6)$$

$I'$ ,  $\phi$  and  $K$  refer here to the quantities given in Tables 1, 2 and 3 respectively,  $M$  is the molecular weight and  $T$  °K the absolute temperature. The summation is for the same molecular formula as is used to express  $K$ . For instance in the case of

$$K_1 = \frac{[\text{CO}] [\text{O}_2]^{1/2}}{[\text{CO}_2]}$$

$$\Sigma M \left( \phi - \frac{I'}{T} \right) \equiv 28 \left( \phi - \frac{I'}{T} \right)_{\text{CO}} + \frac{32}{2} \left( \phi - \frac{I'}{T} \right)_{\text{O}_2} - 44 \left( \phi - \frac{I'}{T} \right)_{\text{CO}_2}$$

3.63. A recent monograph by Lutz<sup>14</sup> gives similar values for the equilibrium constants. They are in fairly good agreement with Table 3 ( $\pm 10$  per cent), with the exception of  $K_3$ . This discrepancy is probably the result of the different value taken for  $\Delta E_0$  in the OH reaction with  $\text{H}_2$  and  $\text{H}_2\text{O}$ .

3.7. In view of the high temperatures under consideration, no corrections have been applied to take into account any deviations from the perfect gas law.

## REFERENCES

- | No. | Author   | Title, etc.   |
|-----|--|---|
| 1   | A. B. P. Beeton .. .. .                          | An Approximate Method for Estimating the Performance of Oxygen-oil Rockets. R. & M. 2389. June, 1946.   |
| 2   | A. R. Gordon .. .. .                             | Thermodynamic Properties of Steam at High Temperatures. <i>J. Chem. Phys.</i> 2, 1934, pp. 64 and 549.  |
| 3   | L. S. Kassel .. .. .                             | Thermodynamic Functions of Carbon Dioxide. <i>J. Amer. Chem. Soc.</i> 56, 1934, p. 1838.  |
| 4   | H. L. Johnston and M. K. Walker                  | Heat Capacity, Entropy and Free Energy of Gaseous Oxygen from Near Abs. Zero to 5000 °K. <i>J. Amer. Chem. Soc.</i> 55, 1933, p. 173; <i>ibid.</i> 57, 1935, p. 682.                                      |
| 5   | H. L. Johnston and D. H. Dawson                  | Heat Capacity, Entropy and Free Energy of Neutral OH from Abs. zero to 5000 °K. <i>J. Amer. Chem. Soc.</i> 55, 1933, p. 2744.   |
| 6   | J. O. Clayton and W. F. Giaque..                 | Heat Capacity and Entropy of Carbon Monoxide: Free Energy to 5000 °K from Spectroscopic Data. <i>J. Amer. Chem. Soc.</i> 54, 1932, p. 2610; amended <i>ibid.</i> 55, 1933, p. 5071.                       |
| 7   | H. L. Johnston and C. O. Davis ..                | Entropy and Heat Capacity of Carbon Monoxide from Near Abs. Zero to 5000 °K. <i>J. Amer. Chem. Soc.</i> 56, 1934, p. 271.   |
| 8   | W. F. Giaque .. .. .                             | The Entropy of Hydrogen and the Third Law of Thermodynamics: the Free Energy and Dissociation of Hydrogen. <i>J. Amer. Chem. Soc.</i> 52, 1930, p. 4816.  |
| 9   | C. O. Davis and H. L. Johnston ..                | Heat Capacity of Hydrogen at High Temperatures: Entropy and Total Energy: a Corrected Table of the Free Energy above 2000° K. <i>J. Amer. Chem. Soc.</i> 56, 1934, p. 1045.                               |
| 10  | H. L. Johnston and M. K. Walker                  | Dissociation of Oxygen up to 5000 °K: the Free Energy of Atomic Oxygen. <i>J. Amer. Chem. Soc.</i> 55, 1933, p. 187; amended <i>ibid.</i> p. 5077.  |
| 11  | E. Justi .. .. .                                 | Spezifische Wärme, Enthalpie, Entropie und Dissoziation Technischer Gase. 1938.   |
| 12  | Wagman, Kilpatrick, Taylor, Pitzer, and Rossini. | Heats, Free Energies and Equilibrium Constants of Some Reactions Involving $\text{O}_2$ , $\text{H}_2$ , $\text{H}_2\text{O}$ , C, CO, $\text{CO}_2$ and CHn. <i>Bur. Stds. J. Res.</i> 34, 1945, p. 143. |
| 13  | R. J. Dwyer and O. Oldenberg ..                  | Dissociation of $\text{H}_2\text{O}$ into H + OH. <i>J. Chem. Phys.</i> 12, 1944, p. 351.   |
| 14  | O. Lutz .. .. .                                  | Technische Thermodynamik dissozierender Gasmische. L.F.A. Völkenrode technical monographs. Publ. 1946.  |

TABLE 1  
*Values of Absolute Total Heat*

T (°K)	I' : C.H.U./lb							
	H <sub>2</sub> O	CO <sub>2</sub>	O <sub>2</sub>	CO	H <sub>2</sub>	OH	O	H
0	0	0	0	2384	28,550	2255	3662	79,850
1500	766	387	368	2791	33,895	2894	4140	87,300
1600	829	419	395	2822	34,285	2941	4171	87,800
1700	893	451	423	2852	34,680	2989	4202	88,290
1800	958	483	451	2883	35,080	3037	4233	88,790
1900	1023	516	479	2913	35,480	3086	4264	89,290
2000	1090	549	507	2944	35,885	3135	4295	89,780
2100	1158	582	535	2974	36,295	3185	4326	90,280
2200	1226	615	564	3005	36,710	3234	4358	90,770
2300	1295	648	593	3037	37,130	3284	4389	91,270
2400	1365	682	621	3068	37,550	3334	4420	91,760
2500	1435	716	650	3100	37,975	3385	4451	92,260
2600	1506	750	679	3132	38,400	3435	4483	92,760
2700	1577	784	708	3164	38,825	3486	4514	93,250
2800	1649	818	737	3196	39,255	3537	4545	93,750
2900	1721	852	767	3228	39,690	3589	4576	94,250
3000	1793	886	797	3260	40,125	3641	4607	94,740
3100	1865	920	827	3191	40,565	3693	4638	95,240
3200	1937	954	857	3323	41,005	3745	4669	95,740
3300	2010	988	887	3355	41,450	3797	4701	96,230
3400	2083	1023	917	3387	41,900	3850	4732	96,730
3500	2156	1058	947	3419	42,350	3903	4764	97,230
3600	2229	1093	977	3452	42,800	3956	4795	97,720
3700	2302	1128	1008	3484	43,255	4009	4827	98,220
3800	2375	1163	1039	3517	43,710	4063	4859	98,720
3900	2449	1198	1070	3549	44,165	4117	4890	99,210
4000	2523	1233	1101	3582	44,625	4171	4922	99,710

**TABLE 2**  
*Values of Absolute Entropy at 1 atm*

T (°K)	$\phi$ : C.H.U./lb/°C							
	H <sub>2</sub> O	CO <sub>2</sub>	O <sub>2</sub>	CO	H <sub>2</sub>	OH	O	H
1500	3.321	1.5875	1.927	2.123	21.37	3.268	2.915	35.43
1600	3.361	1.6080	1.945	2.142	21.62	3.299	2.935	35.75
1700	3.400	1.6275	1.962	2.160	21.86	3.328	2.954	36.05
1800	3.437	1.6460	1.978	2.178	22.09	3.355	2.972	36.34
1900	3.473	1.6635	1.993	2.195	22.30	3.382	2.989	36.60
2000	3.507	1.6805	2.007	2.211	22.51	3.407	3.005	36.86
2100	3.540	1.6965	2.021	2.226	22.71	3.431	3.020	37.10
2200	3.572	1.7125	2.034	2.240	22.90	3.454	3.035	37.33
2300	3.603	1.7275	2.047	2.254	23.09	3.476	3.049	37.55
2400	3.632	1.7420	2.059	2.267	23.27	3.497	3.062	37.76
2500	3.661	1.7560	2.071	2.280	23.44	3.518	3.075	37.97
2600	3.689	1.7695	2.082	2.292	23.61	3.538	3.087	38.16
2700	3.716	1.7825	2.093	2.304	23.77	3.557	3.099	38.35
2800	3.742	1.7950	2.014	2.315	23.93	3.576	3.110	38.53
2900	3.767	1.8070	2.114	2.326	24.08	3.594	3.121	38.70
3000	3.791	1.8185	2.124	2.337	24.23	3.612	3.131	38.87
3100	3.814	1.8295	2.134	2.347	24.37	3.629	3.141	39.04
3200	3.837	1.8405	2.144	2.357	24.51	3.645	3.151	39.19
3300	3.859	1.8510	2.153	2.367	24.65	3.661	3.161	39.35
3400	3.880	1.8610	2.162	2.377	24.78	3.677	3.170	39.50
3500	3.901	1.8710	2.171	2.386	24.91	3.692	3.180	39.64
3600	3.922	1.8805	2.179	2.395	25.04	3.707	3.189	39.78
3700	3.942	1.8900	2.188	2.404	25.17	3.722	3.197	39.91
3800	3.962	1.8990	2.196	2.413	25.29	3.736	3.206	40.05
3900	3.981	1.9080	2.204	2.422	25.41	3.750	3.214	40.18
4000	4.000	1.9170	2.212	2.430	25.53	3.764	3.222	40.30

**TABLE 3**  
*Values of Equilibrium Constants*  
*(Partial pressures in atmospheres)*

$T$ (°K)	$K_1$	$K_2$	$K_3$	$K_4$	$K_5$
	$\frac{[\text{CO}][\text{O}_2]^{1/2}}{[\text{CO}_2]}$	$\frac{[\text{H}_2][\text{O}_2]^{1/2}}{[\text{H}_2\text{O}]}$	$\frac{[\text{OH}][\text{H}_2]^{1/2}}{[\text{H}_2\text{O}]}$	$\frac{[\text{H}]}{[\text{H}_2]^{1/2}}$	$\frac{[\text{O}]}{[\text{O}_2]^{1/2}}$
1500	$0.502 \times 10^{-5}$	$1.926 \times 10^{-6}$	$4.394 \times 10^{-7}$	$1.953 \times 10^{-5}$	$4.543 \times 10^{-6}$
1600	$2.058 \times 10^{-5}$	$0.681 \times 10^{-5}$	$1.895 \times 10^{-6}$	$0.599 \times 10^{-4}$	$1.613 \times 10^{-5}$
1700	$0.709 \times 10^{-4}$	$2.076 \times 10^{-5}$	$0.687 \times 10^{-5}$	$1.612 \times 10^{-4}$	$4.942 \times 10^{-5}$
1800	$2.128 \times 10^{-4}$	$0.558 \times 10^{-4}$	$2.154 \times 10^{-5}$	$3.899 \times 10^{-4}$	$1.337 \times 10^{-4}$
1900	$0.568 \times 10^{-3}$	$1.349 \times 10^{-4}$	$5.985 \times 10^{-5}$	$0.861 \times 10^{-3}$	$3.262 \times 10^{-4}$
2000	$1.368 \times 10^{-3}$	$2.987 \times 10^{-4}$	$1.500 \times 10^{-4}$	$1.758 \times 10^{-3}$	$0.728 \times 10^{-3}$
2100	$3.012 \times 10^{-3}$	$0.614 \times 10^{-3}$	$3.446 \times 10^{-4}$	$3.358 \times 10^{-3}$	$1.506 \times 10^{-3}$
2200	$0.616 \times 10^{-2}$	$1.181 \times 10^{-3}$	$0.734 \times 10^{-3}$	$0.605 \times 10^{-2}$	$2.918 \times 10^{-3}$
2300	$1.184 \times 10^{-2}$	$2.153 \times 10^{-3}$	$1.466 \times 10^{-3}$	$1.036 \times 10^{-2}$	$0.534 \times 10^{-2}$
2400	$2.148 \times 10^{-2}$	$3.735 \times 10^{-3}$	$2.763 \times 10^{-3}$	$1.698 \times 10^{-2}$	$0.929 \times 10^{-2}$
2500	$3.705 \times 10^{-2}$	$0.620 \times 10^{-2}$	$4.957 \times 10^{-3}$	$2.679 \times 10^{-2}$	$1.548 \times 10^{-2}$
2600	$0.613 \times 10^{-1}$	$0.993 \times 10^{-2}$	$0.852 \times 10^{-2}$	$4.079 \times 10^{-2}$	$2.480 \times 10^{-2}$
2700	$0.977 \times 10^{-1}$	$1.534 \times 10^{-2}$	$1.406 \times 10^{-2}$	$0.602 \times 10^{-1}$	$3.838 \times 10^{-2}$
2800	$1.503 \times 10^{-1}$	$2.298 \times 10^{-2}$	$2.235 \times 10^{-2}$	$0.866 \times 10^{-1}$	$0.576 \times 10^{-1}$
2900	$2.247 \times 10^{-1}$	$3.345 \times 10^{-2}$	$3.440 \times 10^{-2}$	$1.213 \times 10^{-1}$	$0.841 \times 10^{-1}$
3000	0.3280	0.0476	0.0516	0.1665	0.1197
3100	0.4678	0.0662	0.0755	0.2239	0.1664
3200	0.6520	0.0904	0.1078	0.2957	0.2268
3300	0.8890	0.1212	0.1510	0.3840	0.3034
3400	1.193	0.1601	0.2075	0.4907	0.3989
3500	1.574	0.2080	0.2796	0.6190	0.5165
3600	2.047	0.2660	0.3705	0.7705	0.6590
3700	2.615	0.3354	0.4826	0.9485	0.8305
3800	3.300	0.4185	0.6220	1.155	1.034
3900	4.110	0.5163	0.7905	1.392	1.273
4000	5.057	0.6308	0.9925	1.663	1.550



PART II

# The Effect of Dissociation on Rocket Performance Calculations

By

F/LT. A. B. P. BEETON

*Summary.*—The equilibrium constants and thermal properties of all the important gas components have been used to calculate some theoretical combustion chamber temperatures and specific impulses allowing for all dissociation effects. The results are compared with a previous method which ignored dissociation (into OH, O and H components), in the case of a propellant consisting of a 3 to 1 mixture ratio of oxygen and hydrocarbon fuel.

The combustion chamber temperature is found to be about 300°C lower and the specific impulse about 10 seconds smaller than the figures given previously.

1. *Scope of Present Calculations.*—1.1. The method used in R. & M. 2389<sup>1</sup> has been extended to allow for the products of dissociation at high temperatures. These products, the existence of which was previously ignored, are OH, O and H.

1.2. The thermal data pertaining to all ordinarily possible combustion products containing carbon, hydrogen and oxygen only has recently been reviewed in Part I of this report and the most reliable values tabulated for every 100° over the interval 1500° to 4000°. The quantities given are the absolute entropy at 1 atm and the absolute total heat per unit mass, referred to CO<sub>2</sub>, H<sub>2</sub>O and O<sub>2</sub> as the substances of zero energy content. The equilibrium constants concerned, which may be calculated from these values, are also tabulated as functions of temperature.

1.3. In view of the much larger amount of calculation involved when the additional dissociation products are considered, the present exact analysis has been limited to a single mixture ratio, namely 3 to 1 by weight of oxygen to fuel. The chemically-correct ratio would be 3.465 to 1 for the fuel considered.

1.4. For this mixture ratio, a Mollier diagram over the appropriate range of temperature and pressure has been constructed from the data given in the first part of this report. This enables values for the specific impulses and gas temperatures to be plotted as functions of the combustion chamber pressure for isentropic expansion down to 1 atm exit pressure.

1.5. The values obtained in this way are compared with those given previously in R. & M. 2389<sup>1</sup>, and also with the results given by the assumption that the expansion process is sufficiently rapid to prevent any change in mixture composition between combustion chamber and outlet conditions.

2. *Outline of Method.*—2.1. As already mentioned, the present exact calculation is based on the same method as used in R. & M. 2389<sup>1</sup>, extended to take into account the additional variables.

2.2. The three extra unknowns introduced by the expressions for the partial pressures of OH, O and H are solved by the three additional equilibrium constants which are now applicable,

$$K_3 = \frac{[\text{OH}] [\text{H}_2]^{1/2}}{[\text{H}_2\text{O}]}$$

$$K_4 = \frac{[\text{H}]}{[\text{H}_2]^{1/2}}$$

and

$$K_5 = \frac{[\text{O}]}{[\text{O}_2]^{1/2}}$$

2.3. The solution of the equations is not unduly laborious if solved for given values of the temperature  $T$  and of the partial pressure of oxygen  $[O_2]$ . Total heat and entropy are calculated as in Ref. 1, enabling the isothermal lines to be plotted directly on a Mollier diagram. The lines of constant total pressure are added later by graphical interpolation.

2.4. To obtain points on the line  $P = 1$  atmosphere, it is necessary to take a given temperature in the probable range (in this case 2600 to 2900 °K), and to guess a suitable value of  $[O_2]$  which will give a total pressure in the neighbourhood of 1 atmosphere when all the partial pressures are evaluated. Three or four sets of values are found, and all pressures are plotted against  $[O_2]$  or  $[O_2]^{1/2}$ . Interpolation for the total pressure  $P = 1$  atmosphere then gives the required partial pressures, from which the proportions by weight, total heats and entropies may be calculated in the usual manner.

2.5. The further calculation referred to in section 1.5 assumes that dissociation is 'frozen' at combustion chamber conditions throughout the expansion.

2.51. Interpolation between points already evaluated on an isothermal gives the values of the total pressures and of the various partial pressures at the particular point having the required initial total heat. We now assume that the proportions by weight do not alter, and so the quantity

$$\Sigma \frac{mG}{M} \log_e P'$$

may be evaluated for the condition  $\Sigma P' = 1$  atmosphere. The notation in the above expression is

- $P'$  partial pressure (atm. abs.)
- $M$  molecular weight
- $m$  proportion by weight
- $G$  universal gas constant = 1.986 C.H.U./lb mol wt/°C.

2.52. We next have to assume an outlet temperature, look up the values of the entropy  $\phi$  for the various components at this temperature, and work out  $\Sigma m\phi$ . The entropy of the mixture is then given by

$$\Phi = \Sigma m\phi - \Sigma \frac{mG}{M} \log_e P',$$

as shown in Ref. 1. We then work out a few more values for different outlet temperatures and interpolate for the required entropy value for isentropic expansion. With the outlet temperature now determined,  $\Sigma mI'$  is then worked out for two or three integral temperatures in the neighbourhood of this temperature, and  $\Sigma mI'$  at outlet found by interpolation.

2.53. We therefore have simultaneous values for the initial total pressure in the combustion chamber, for the isentropic heat drop and for the outlet gas temperature. These values are used to calculate the performance with 'frozen' equilibrium.

3. *Presentation of Results.*—3.1. The total heat-entropy diagram as calculated by the exact method is shown in Fig. 1. The line corresponding to the total heat of the propellants fed in is taken as 2577 C.H.U./lb, which was the value shown in Ref. 1 to correspond to the heat content of pure liquid oxygen at  $-183$  °C and a typical hydrocarbon fuel at  $25$  °C in the ratio 3 to 1 by weight.

3.2. Similar diagrams have been published before, and examples may be found in Refs. 3 and 4. These published results do not, however, give the basic data on which the diagrams are worked out, or any details regarding the method of calculation. The results, where comparable, are in moderately good agreement with those given in this note.

3.3. The specific impulse calculated from the Mollier diagram assuming isentropic expansion down to 1 atmosphere outlet pressure is plotted against the initial pressure in Fig. 2. Another curve is given showing the variation of specific impulse as calculated by the approximate method of Ref. 1, which neglects dissociation into OH, O and H. The third curve shows the specific impulse calculated on the assumption of 'frozen' conditions as outlined in section 2.51 to 2.53.

3.4. In Fig. 3, the maximum combustion chamber temperatures given by  $\Sigma mI' = 2577$  in Fig. 1 are plotted against the pressure. A further curve shows the same quantity as found by the approximate method for this mixture ratio.

3.5. Finally Fig 4 gives the calculated gas temperatures at outlet after isentropic expansion down to 1 atm final pressure. The three curves correspond to the same three cases as taken in Fig. 2.

4. *Examination of Results.*—4.1. Compared with the approximate method of Ref. 1, the present exact method is seen from Fig. 2 to give calculated specific impulses about 10 sec lower than before over the range 10 to 60 atm combustion chamber pressure for the mixture-ratio under consideration (3 to 1). The lower value is mainly the result of the inferior thermodynamic efficiency which is caused by the lower combustion chamber temperatures found when dissociation is fully taken into account. There is also a loss due to the amount of energy still latent as heat of dissociation at the outlet condition.

4.2. In the case of 'frozen' equilibrium, the relatively large proportions of OH, O and H components under combustion chamber conditions are assumed to persist right through the expansion. This means that a considerable proportion of the energy remains locked up as heat of dissociation, and is not available to contribute to the kinetic energy of the gases. Consequently the specific impulse in this case comes out considerably lower than when equilibrium conditions are assumed throughout, as in the 'accurate' calculation. The difference is about 10 sec for 10 atm and 17 sec for 60 atm combustion chamber pressure.

4.3. Fig. 3 shows that the reduction in combustion chamber temperature found by applying the more accurate analysis amounts to about 300 °C over the usual pressure range.

4.4. The outlet gas temperature as given in Fig. 4 does not appear to be greatly altered by taking dissociation into account. The greater part of the heat quantity required to provide the equilibrium dissociation (which is not very great under outlet conditions), is in fact available by virtue of the smaller amount of heat converted into kinetic energy.

4.5. As would be expected, the outlet temperature calculated for the case of 'frozen' equilibrium is very much lower, since the whole of the kinetic energy in this case has to be provided by  $C_p \cdot \Delta T$ . The actual difference in the calculated outlet temperatures varies according to the initial pressure, but is of the order of 750 °C (at 20 atm, 2000 °K instead of 2750 °K).

4.6. Fig. 2 shows that allowing for dissociation does not have a great deal of effect on the variation of specific impulse with combustion chamber pressure. The increase in specific impulse on raising the pressure from 20 to 60 atm remains between 14 and 15 per cent whichever of the three curves shown in Fig. 2 is taken.

5. *Comparison with Actual Tests.*—5.1. Little reliable information has yet been published on quantitative experimental investigations into the performance of oxygen rockets. Ref. 4 contains a certain number of test results.

5.2. The best combustion chamber tested in Ref. 4 gives the following spot point with diesel oil and gaseous oxygen:

Chamber pressure	..	..	..	..	40 ata. (38.7 atm)
Mixture ratio	..	..	..	..	3 to 1
Exhaust velocity	..	..	..	..	2570 m/sec
therefore Specific impulse	..	..	..	..	262 sec.

The equivalent condition gives a specific impulse of 278 sec calculated by the accurate method and assuming liquid oxygen used. The correction from liquid to gaseous oxygen amounts to about  $2\frac{1}{2}$  sec under these conditions, making the calculated specific impulse  $280\frac{1}{2}$  sec. The test value is, therefore,  $18\frac{1}{2}$  sec less than the calculated value.

5.3. The specific impulse evaluated on the assumption of 'frozen' equilibrium is 264 sec for the test quoted above from Ref. 4. This brings the calculated value almost exactly into agreement with the observed value. It is not, however, to be taken as proving the validity of the assumption of 'frozen' conditions, but rather the reverse, since it is impossible to believe that there will be no losses in the actual rocket chamber.

5.4. Losses will probably arise from the following effects:—

- (i) Poor distribution, giving non-uniform conditions over the section of the flow. This has the effect of making parts of the mixture too rich and other parts too weak, both of which conditions are likely to result in a reduced specific impulse.
- (ii) Friction, turbulence and the formation of shock waves in the gas stream.
- (iii) Loss of heat to the walls during expansion. In the case of a regeneratively cooled system, when the heat so extracted is returned to the liquid propellants, it is possible that a slight thermodynamic *advantage* may arise due to this effect, which is analogous to the 'bleeding' process applied to the classical steam-engine cycle.

6. *Conclusions.*—6.1. For the case examined, namely 3 to 1 mixture ratio by weight of liquid oxygen to hydrocarbon fuel, the effect of considering the dissociated components OH, O and H is to cause a decrease of about 10 sec in the calculated specific impulse.

6.2. The corresponding effect on the calculated combustion chamber temperature is a reduction of about 300 °C. The effect on the gas outlet temperature is relatively small, less than 100 °C.

6.3. Allowing for dissociation does not appreciably alter the rate of increase of specific impulse with the combustion chamber pressure.

6.4. If the expansion is assumed to be sufficiently rapid so as effectively to 'freeze' dissociation throughout the expansion at the conditions obtaining in the combustion chamber, then a further reduction in specific impulse is calculated to occur. This amounts to between 10 and 17 sec depending on the combustion chamber pressure.

6.5. The gas outlet temperature affords a good indication of the extent to which these non-equilibrium conditions occur. The calculated difference between the 'fully-equilibrium' and 'fully-frozen' cases is of the order of 750 °C.

6.6. It seems likely that the exact calculated specific impulses will come out about 20 sec higher than test figures, though there is as yet insufficient published experimental data to enable a fair comparison to be made. The value calculated on the assumption of 'frozen' equilibrium seems to agree very well with observed values, but this is probably a coincidence due to unaccounted-for losses approximately counteracting the unduly pessimistic theoretical values found on this assumption.

## REFERENCES

No.	Author	Title, etc.
1	A. B. P. Beeton .. ..	An Approximate Method for Estimating the Performance of Oxygen-oil Rockets. R. & M. 2389. June, 1946.
2	A. B. P. Beeton .. ..	Tabulated Thermal Data for Hydrocarbon Oxidation Products at High Temperatures. A.R.C.10171. October, 1946. Part I of this report.)
3	M. von Stein .. ..	Verfahren zur Berechnung der Flammentemperaturen, der Enthalpie und Entropie von Feuergasen. Forschung auf dem Gebiete des Ingenieurwesens, Vol. 14, No. 5. September, 1943.
4	Ziebland .. ..	Bericht über Versuche mit Raketenbrennkammern für Sauerstoff und Gasöl. Published in translation as H.E.C. 552. (November, 1944.)

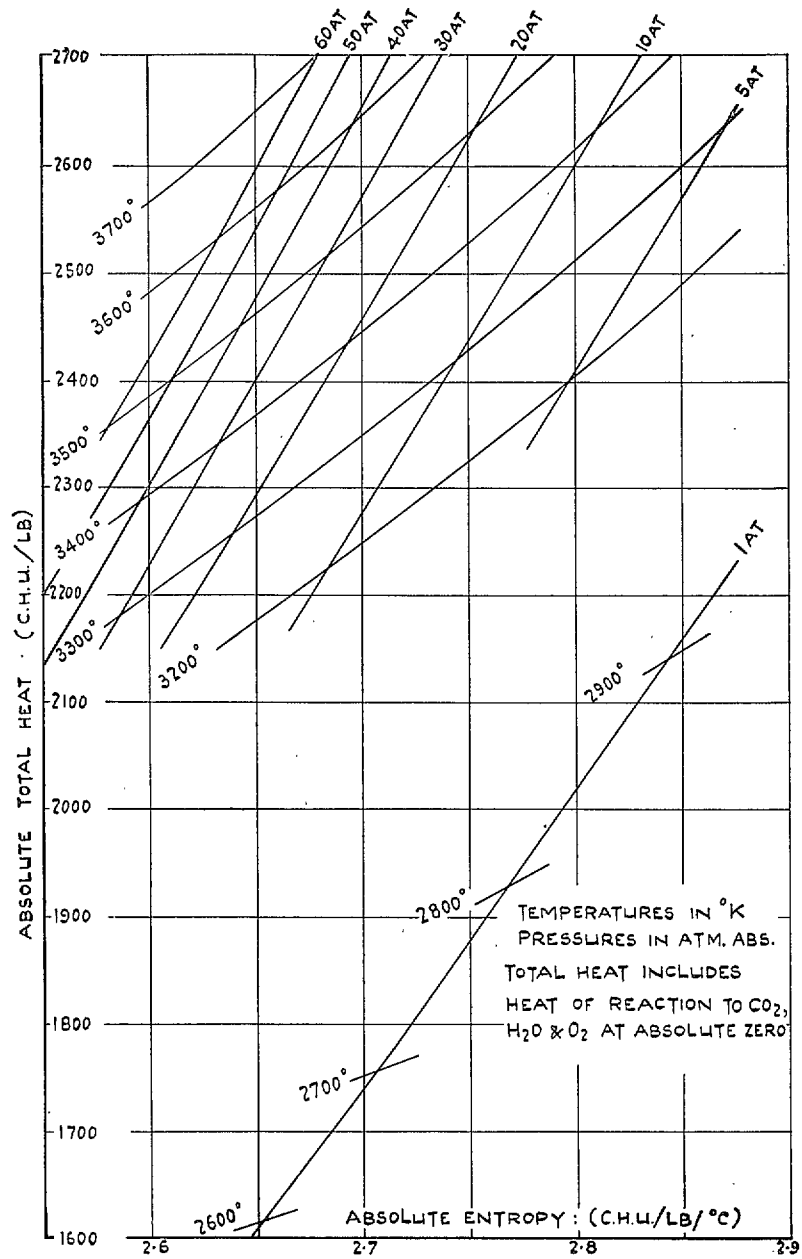


FIG. 1. Calculated Mollier diagram for 3 to 1 ratio.

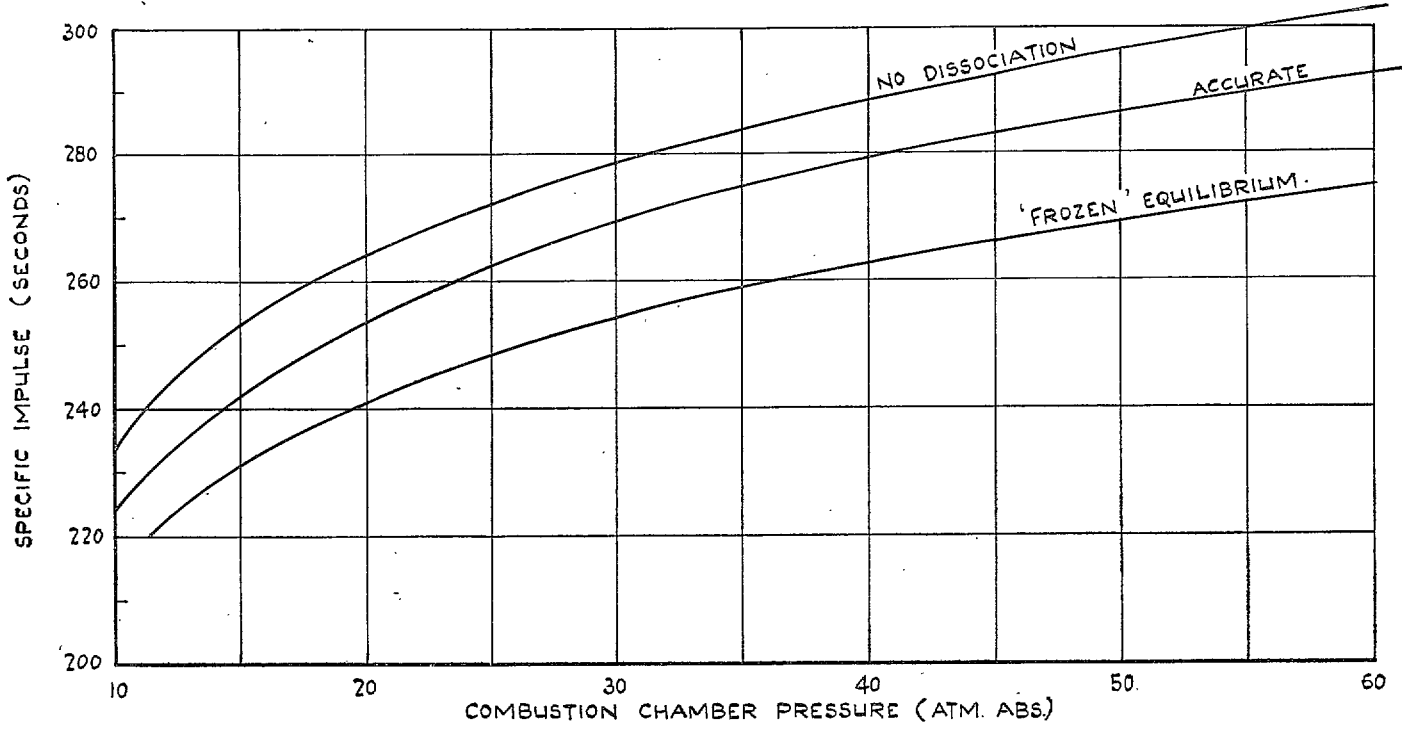


FIG. 2. Calculated specific impulse of LO<sub>2</sub>—Oil rocket.  
 (3 to 1 mixture ratio by weight. Isentropic expansion down to 1 atm)

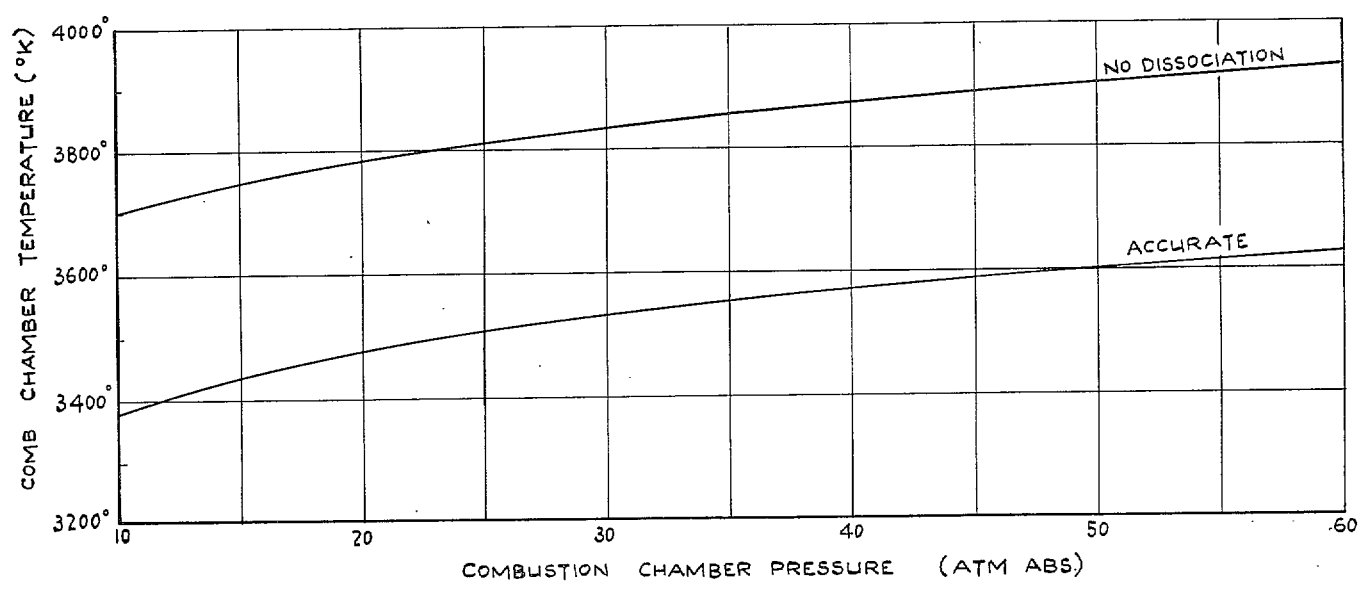


FIG. 3. Calculated combustion—Chamber temperatures (3 to 1 mixture ratio by weight).

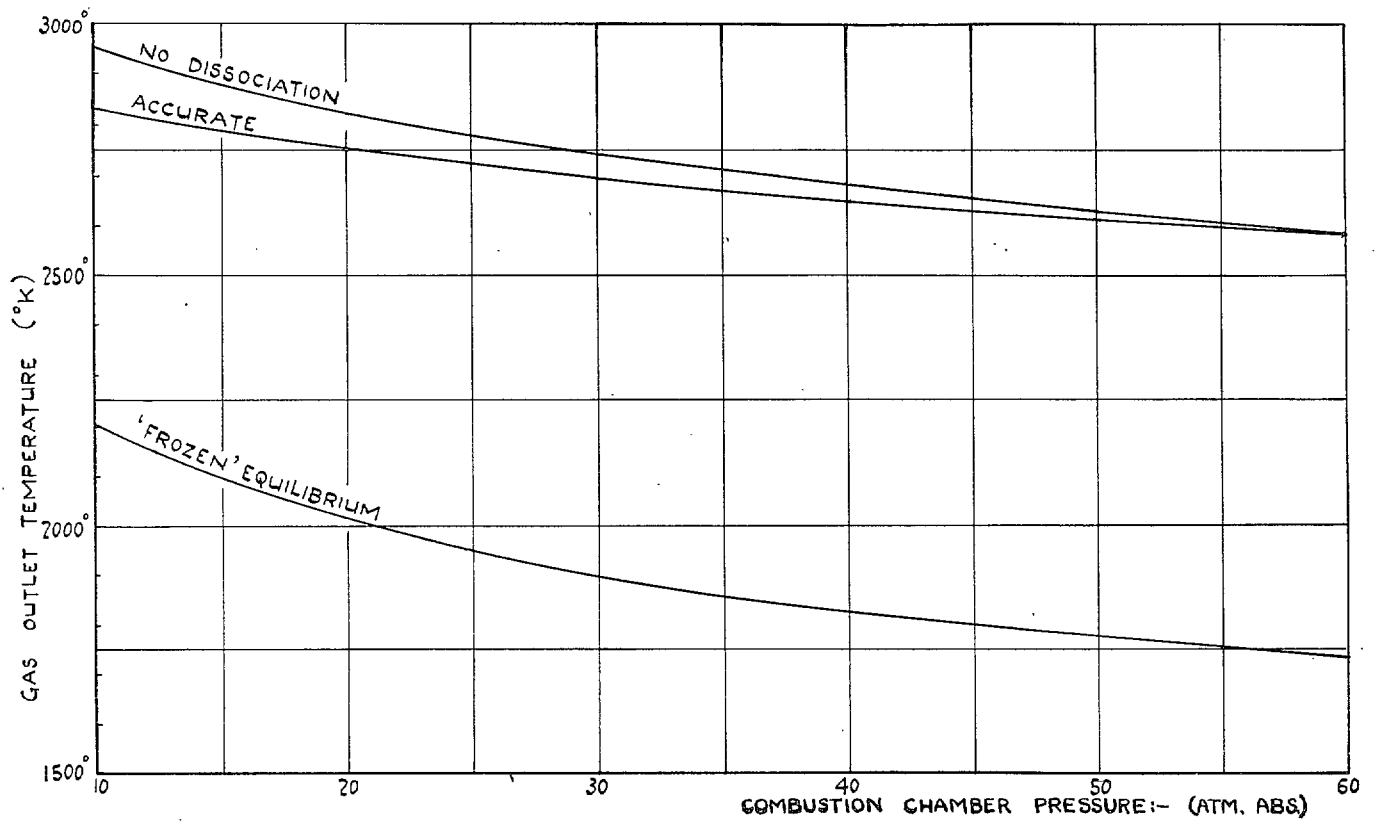


FIG. 4. Calculated gas outlet temperatures.  
(3 to 1 mixture ratio by weight. Isentropic expansion down to 1 atm.)

## Publications of the Aeronautical Research Council

### ANNUAL TECHNICAL REPORTS OF THE AERONAUTICAL RESEARCH COUNCIL (BOUND VOLUMES)—

- 1934-35 Vol. I. Aerodynamics. *Out of print.*  
Vol. II. Seaplanes, Structures, Engines, Materials, etc. 40s. (40s. 8d.)
- 1935-36 Vol. I. Aerodynamics. 30s. (30s. 7d.)  
Vol. II. Structures, Flutter, Engines, Seaplanes, etc. 30s. (30s. 7d.)
- 1936 Vol. I. Aerodynamics General, Performance, Airscrews, Flutter and Spinning.  
40s. (40s. 9d.)  
Vol. II. Stability and Control, Structures, Seaplanes, Engines, etc. 50s. (50s. 10d.)
- 1937 Vol. I. Aerodynamics General, Performance, Airscrews, Flutter and Spinning.  
40s. (40s. 10d.)  
Vol. II. Stability and Control, Structures, Seaplanes, Engines, etc. 60s. (61s.)
- 1938 Vol. I. Aerodynamics General, Performance, Airscrews. 50s. (51s.)  
Vol. II. Stability and Control, Flutter, Structures, Seaplanes, Wind Tunnels,  
Materials. 30s. (30s. 9d.)
- 1939 Vol. I. Aerodynamics General, Performance, Airscrews, Engines. 50s. (50s. 11d.)  
Vol. II. Stability and Control, Flutter and Vibration, Instruments, Structures,  
Seaplanes, etc. 63s. (64s. 2d.)
- 1940 Aero and Hydrodynamics, Aerofoils, Airscrews, Engines, Flutter, Icing, Stability  
and Control, Structures, and a miscellaneous section. 50s. (51s.)

*Certain other reports proper to the 1940 volume will subsequently be  
included in a separate volume.*

### ANNUAL REPORTS OF THE AERONAUTICAL RESEARCH COUNCIL—

1933-34	1s. 6d. (1s. 8d.)
1934-35	1s. 6d. (1s. 8d.)
April 1, 1935 to December 31, 1936.	4s. (4s. 4d.)
1937	2s. (2s. 2d.)
1938	1s. 6d. (1s. 8d.)
1939-48	3s. (3s. 2d.)

### INDEX TO ALL REPORTS AND MEMORANDA PUBLISHED IN THE ANNUAL TECHNICAL REPORTS, AND SEPARATELY—

April, 1950 R. & M. No. 2600. 2s. 6d. (2s. 7½d.)

### INDEXES TO THE TECHNICAL REPORTS OF THE AERONAUTICAL RESEARCH COUNCIL—

December 1, 1936 — June 30, 1939.	R. & M. No. 1850. 1s. 3d. (1s. 4½d.)
July 1, 1939 — June 30, 1945.	R. & M. No. 1950. 1s. (1s. 1½d.)
July 1, 1945 — June 30, 1946.	R. & M. No. 2050. 1s. (1s. 1½d.)
July 1, 1946 — December 31, 1946.	R. & M. No. 2150. 1s. 3d. (1s. 4½d.)
January 1, 1947 — June 30, 1947.	R. & M. No. 2250. 1s. 3d. (1s. 4½d.)

*Prices in brackets include postage.*

Obtainable from

### HER MAJESTY'S STATIONERY OFFICE

York House, Kingsway, LONDON, W.C.2 423 Oxford Street, LONDON, W.1  
P.O. Box 569, LONDON, S.E.1  
13a Castle Street, EDINBURGH, 2 1 St. Andrew's Crescent, CARDIFF  
39 King Street, MANCHESTER, 2 Tower Lane, BRISTOL, 1  
2 Edmund Street, BIRMINGHAM, 3 80 Chichester Street, BELFAST

or through any bookseller.