The Measurement of the Specific Enthalpy of Steam at Pressures of 60 to 1000 Bar and Temperatures of 400 to 700 degrees C

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THE MEASUREMENT OF THE SPECIFIC ENTHALPY OF STEAM AT PRESSURES OF 60 TO 1000 BAR AND TEMPERATURES OF 400 TO 700 °C

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CONTENTS

The specific enthalpy of steam has been measured by a continuous flow method at pressures from 60 to 1000 bar and at temperatures from 400 to 700 °C.

Steam was generated in an electrically heated single-tube flash boiler and, after its pressure and temperature had been measured, was expanded adiabatically into a condenser-calorimeter through which flowed a stream of cooling water. Measurements were made of the temperatures of the condensed steam and of the incoming and outgoing streams of cooling water and of the rate of flow of the condensate. From this, an energy balance was drawn up and the apparent enthalpy of steam determined. The connexion between the enthalpy of steam and the apparent enthalpy measured was related to the rates of flow of the condensate and cooling water, and from a series of experiments in which these rates were varied an empirical correlating equation was established from which the enthalpy of steam could be derived.

The accuracy of the results, taking into account the errors both of the measurements and of the correlating equations, is estimated to be of the order of 0·1 %.

Nomenclature

H	specific[†] enthalpy of steam
H_1	specific enthalpy of steam at pressure P_1 and temperature T_1
H^*_{11}	apparent specific enthalpy of steam corrected to pressure P_1 and temperature T_1
H^*_{00}	apparent specific enthalpy of steam measured at pressure P_0 and temperature T_0

[†] In this paper, the word 'specific' is omitted from the term 'specific enthalpy', where there is no likelihood of misunderstanding.

H_k^*	single apparent specific enthalpy value ($H_{00}^* = \Sigma H_k^*/n$)
h_1	specific enthalpy of outgoing cooling water
h_2	specific enthalpy of incoming cooling water
h_μ	specific enthalpy of condensate
M	cooling water flow rate $= (W_M + \eta_M)/t_M$
P_0	mean pressure at which an experiment was performed
P_1	pressure to which an experimental enthalpy was adjusted
$\Delta P = P_1 - P_0$	
Q	gross heat leak
q	net heat leak
T_0	mean temperature at which an experiment was performed
T_1	temperature to which an experimental enthalpy was adjusted
$\Delta T = T_1 - T_0$	
t_M	time of collection of cooling water
t_μ	time of collection of condensate
W_M	mass of cooling water collected in time t_M
W_μ	mass of condensate collected in time t_μ
ϵ_c	correction to apparent enthalpy for heat exchange between condenser and surroundings
ϵ_s	correction to apparent enthalpy for variation with time of heat stored in condenser
η_M	correction to cooling water collection for evaporation loss
θ_1	temperature of outgoing cooling water
θ_2	temperature of incoming cooling water
θ_μ	temperature of condensate

Note on units. The units used are related by

$$1\ \text{bar cm}^3/\text{g} = 0{\cdot}1\ \text{J/g}.$$

1. Introduction

A knowledge of the thermodynamic properties of steam over wide ranges of pressure and temperature is of fundamental importance to power engineers, and many independent investigations have been undertaken in recent years to obtain data of the requisite accuracy by workers in the United States, the U.S.S.R., the United Kingdom, Germany and Czecho-Slovakia. The results of this work have from time to time been coordinated by an International Steam Table Conference, and 'Skeleton steam tables' in which each value is accompanied by a 'tolerance' representing its probable accuracy, have been published (Anon 1930, 1931, 1935, 1964). By agreement, any set of steam tables which is thermodynamically consistent, and in which the values fall within the tolerance of the most recent skeleton table, is considered to have international status.

At a meeting of the Conference held in London in 1956 it was proposed to extend the range of the then current '1934 Skeleton steam tables' to meet the more exacting demands of boiler and turbine designers and other users of high-pressure steam, and this action has resulted in the production of much new data, and in the publication of the '1963 Skeleton steam tables'. As part of the experimental programme the measurements on enthalpy reported here were undertaken by a group at the Imperial College, London, financed by the British Electrical and Allied Industries Research Association and latterly by the Central Electricity Generating Board.

In planning the work the limits set were those that would give a substantial overlap with the upper limit of the 1934 Tables and would extend to the highest temperatures and pressures at which observations could be made with reasonable accuracy. The accuracy aimed at was approximately one part in a thousand.

The method employed was essentially that used by Egerton & Callendar (1932) and consisted in expanding steam at a known temperature and pressure through an orifice and subsequently condensing it: the enthalpy is then found from the quantity of heat removed in the condenser together with heat losses from the outlet sections of the plant. In carrying out an experiment raw water is purified and de-aerated before being fed to a high pressure boiler and superheater. Steam leaving the superheater passes through a pocket in which its temperature and pressure are measured, and then expands almost adiabatically through an orifice, and passes into a condenser. The temperatures of the condensed steam and of the inlet and outlet cooling water and the flows of condensate and cooling water are measured.

From these data an energy balance for steady flow through the condenser gives

$$M[(h_1-h_2)+(U_1^2-U_2^2)/2+g(Z_1-Z_2)]+\mu[(h_\mu-H)+(u_\mu^2-u^2)/2+g(z_\mu-z)]=-Q,$$

where U_1, U_2 are the velocities of cooling water at exit and inlet, u_μ, u are the velocities of condensate and steam, respectively, and Z_1, Z_2, z_μ and z are the corresponding altitudes of exits and inlets, and g is gravitational acceleration.

If the apparatus is so arranged that the kinetic and gravitational energy terms are negligible, then

$$\mu(H-h_\mu)=M(h_1-h_2)+Q,$$

thus defining the total or gross heat leak Q. Hence

$$H=(M/\mu)\,(h_1-h_2)+h_\mu+(Q/\mu).$$

The apparent enthalpy of experiment, H_{00}^* may be defined by

$$H_{00}^*=(M/\mu)\,(h_1-h_2)+h_\mu,$$

and the general relation between enthalpy and specific enthalpy is then

$$H=H_{00}^*+Q/\mu,$$

where Q is the overall heat leak and Q/μ is the overall heat leak correction.

2. The apparatus and experimental method

(a) *Materials of construction*

The upper limits of temperature and pressure which are at present attainable by the method used are set by the properties of the materials available for the construction of the boiler, superheater and their connexions. The properties required are high tensile strength with resistance to creep, resistance to corrosion, high electrical resistivity and good machinability. The materials possessing the best combination of these properties are the nickel-chromium alloys known collectively as the Nimonic alloys. For all parts of the plant subject to high pressures and temperatures Nimonic 80 was employed; for all other parts in contact with pure water Nimonic 75 was used.

These alloys were found to be highly resistant to attack by steam and no permanent gases were ever found in the condenser. Furthermore, a metallurgical examination of the superheater tubes after 2000 h running showed no signs of corrosion.

(*b*) *The apparatus*

The general layout of the plant is shown in figure 1.

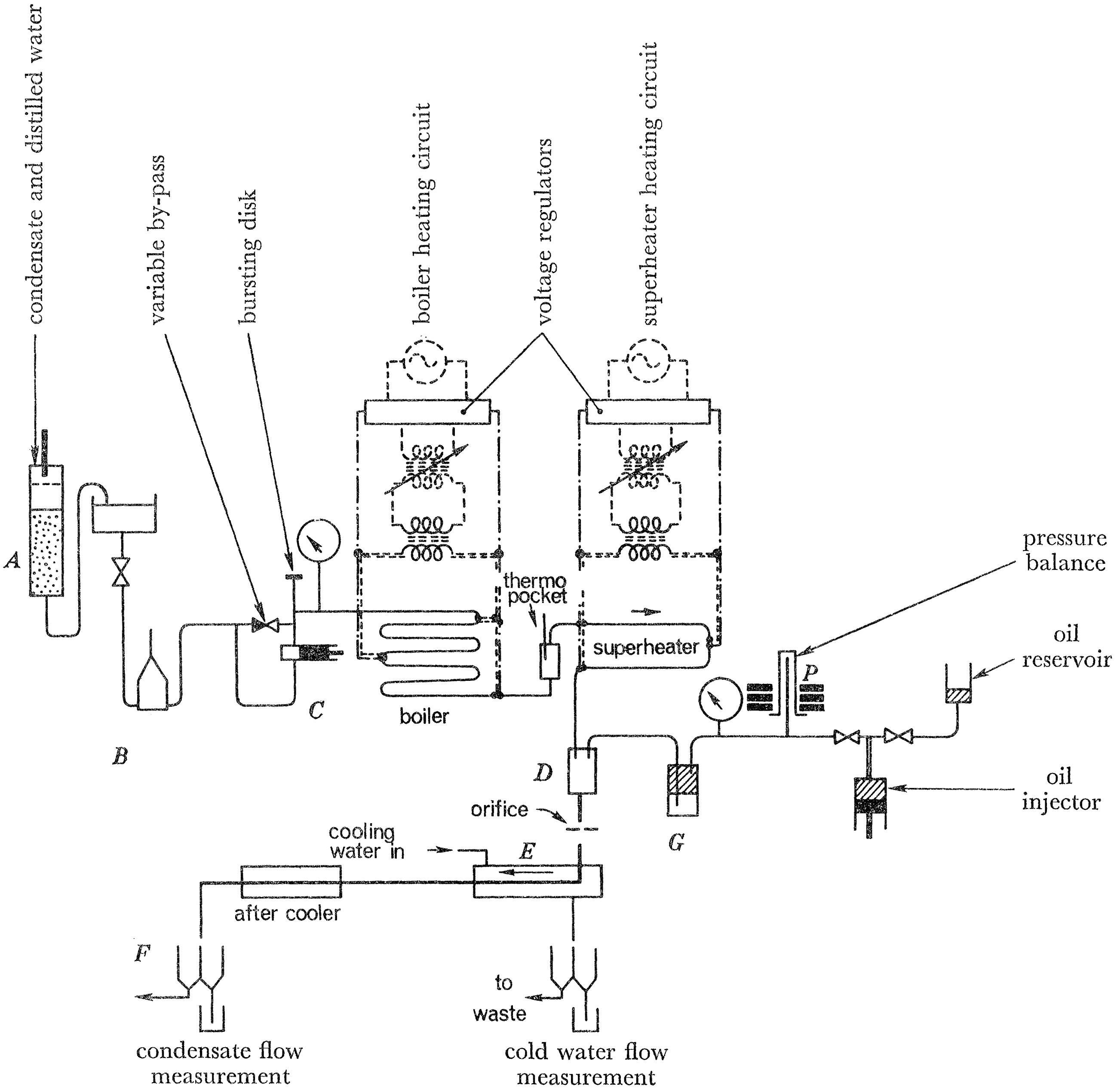

FIGURE 1. Flow diagram of apparatus.

The feed water is prepared from distilled water by passing it first through a bed of mixed de-ionizing resins contained in the column *A*, and thence through two simple de-aerators *B*, in series, which boil away about 5 % of the throughput. The purity of the product is tested from time to time by conductivity measurements and by electro-chemical tests for oxygen.

The water from the de-ionizing column has a resistivity of about 1 MΩcm, and the columns are regenerated whenever it falls below this value. The dissolved oxygen content is generally less than $0{\cdot}01/10^6$.

The water from the de-aerator is cooled and passes to the feed pump *C*, which is a single cylinder reciprocating pump fitted with ball valves. At a pressure of 1000 bar the throughput is about 60 lb./h; the output can be varied by means of a by-pass valve. In general the pump is working against a cushion of steam about 100 ft. long which effectively dissipates any oscillations at the condenser end of the plant.

The boiler consists of eleven Nimonic 80 tubes, each 8 ft. long with outer and inner diameters of $\frac{9}{16}$ and $\frac{3}{16}$ in. respectively, connected in series. Heat is supplied by passing a low voltage alternating current through the walls. When working above the critical point (374 °C) the heating is adjusted so that the steam is brought approximately to the critical temperature in the boiler and the extra heat is supplied by the superheater, thus ensuring that the boiler tubes are not exposed to temperatures at which creep is important.

The boiler tubing is carried on a mobile cradle which is enclosed in a mild steel drum lagged externally.

From the boiler the steam passes through a thermometer pocket into the superheater which consists of a 20 ft. length of tube of the same diameter as the boiler tubes. It is contained in a rectangular steel tank 9 ft. × 2 ft. × 2 ft., filled with exfoliated vermiculite insulating material.

The boiler and superheater heating circuits are similar but of differing outputs. Each is made up of an auto-transformer fed from the mains, connected to a step-down transformer, the output of which is carried by copper busbars to the Nimonic tubing. The auto-transformers are variable; a coarse adjustment can be made by changing links when the plant is off-load, a fine adjustment can be made with an on-load switch. The voltages at the entrance to the boiler and superheater are measured and maintained constant by comparing them with reference voltages and using the out-of-balance voltage to vary a stabilizing transformer which is in circuit between the mains input and the auto-transformer.

The maximum output of the boiler transformer is 37·5 kVA (50 V at 750 A) and that of the superheater transformer 24 kVA (20 V at 1200 A).

On leaving the superheater the steam passes into the vessel *D*, which houses the thermocouple for measuring the temperature before expansion, a connexion to the pressure balance *P*, and the expansion orifice. The orifice consists of a $\frac{1}{4}$ in. thick Nimonic 80 disk pierced by a fine hole through which the steam expands into the condenser. A set of forty disks with holes of diameters from 0·003 to 0·10 in. is available from which to select one appropriate to the conditions required.

The steam expands into a water-cooled shell and tube condenser *E*, which is situated as close as possible to the orifice. The shell is well lagged and the incoming cooling water circulates round the outside of the lagging before entering the tubes. The temperature of the incoming and outgoing water and of the condensate are measured by three platinum resistance thermometers, each of which is placed so that the centre of the bulb is level with the end plate of the condenser, this having been found by experiment to be the position at which the outgoing water stream temperatures are constant and at a maximum for a distance of $2\frac{1}{4}$ in. The thermometers are connected through a selector switch to a Smith's no. 2 Wheatstone bridge (Smith 1912). The general arrangement of the condenser–calorimeter is shown in figure 2.

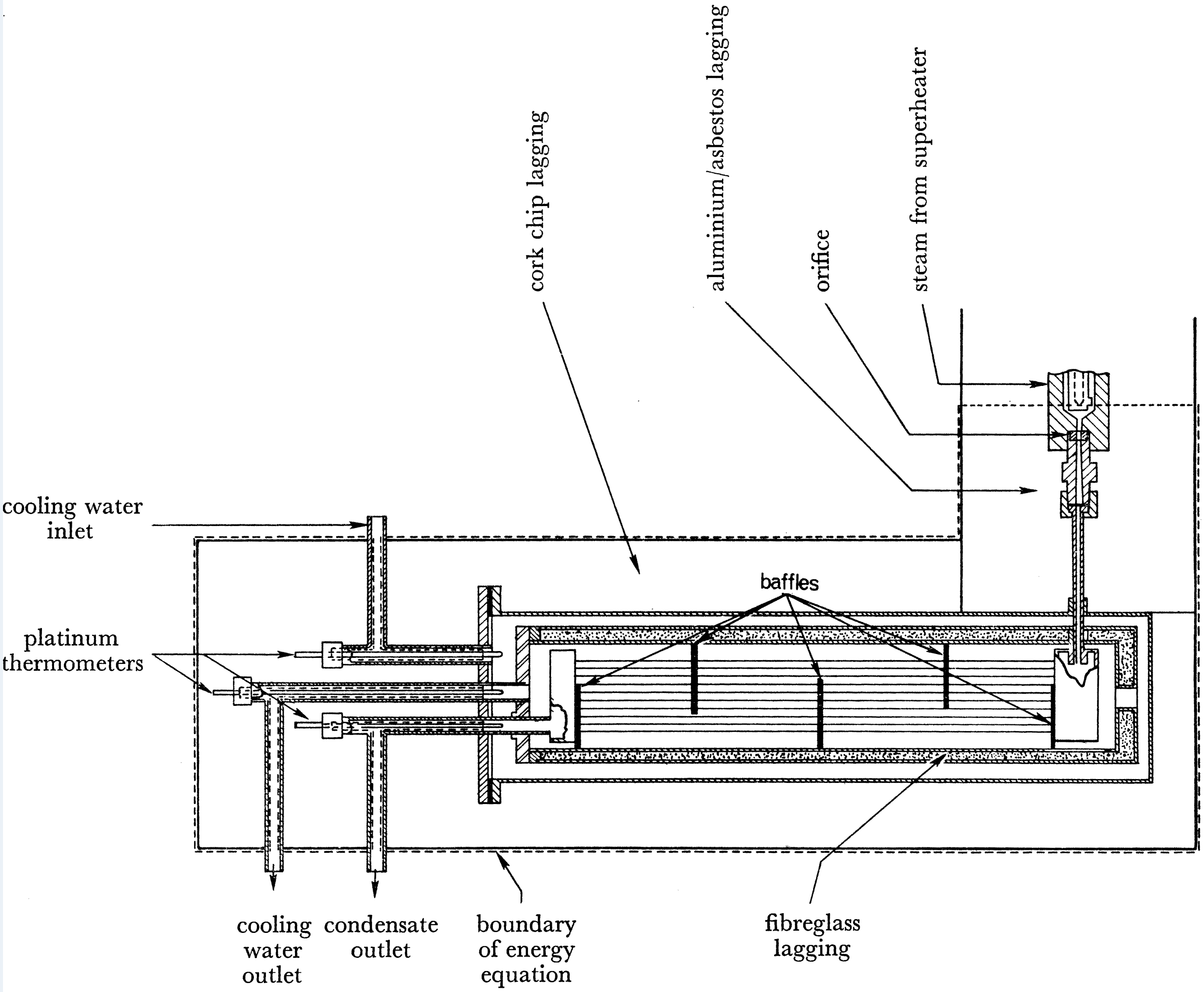

FIGURE 2. Sketch of condenser-calorimeter.

(c) *Measurement of water temperatures*

The three thermometers used were chosen from a batch of six which are all 4-conductor $18\,\Omega$ platinum thermometers with the resistance spiral wound non-inductively on a silica cross 2 in. long. The leads are 10 in. long and the whole is encased in a Pyrex envelope, $\frac{1}{4}$ in. in diameter, filled with helium. Initially all six thermometers were calibrated at the ice, steam and sulphur points by the National Physical Laboratory and one was then kept as a standard.

The effect of the various possible instrument and reading errors have been investigated, together with errors in calibration of the thermometers. The readings of the cooling water thermometers are estimated to have a standard deviation of 0·005 degC, and the standard deviation of the condensate thermometer is estimated to be 0·03 degC; the effect of all three on the apparent enthalpy is to increase its variance by 0·5 $(\mathrm{J/g})^2$.

Account has to be taken of possible variations between the water temperature and the resistance bulb temperature. The thermometer is immersed to a depth of 8 in. in the stream and the tube conveying the stream has a 6 in. thick cork lagging. If the water temperature remains constant the variation should be negligible. There have been several occasions when, while readings were being taken, an abrupt change has occurred in the rate of steam or cooling water flow. In every case the thermometer reading has become stabilized at the new value within half a minute. Since no experiment was accepted unless the changes in all the instrument readings during the experiment were very small, the effect on the temperature readings are negligible.

Usually the cooling water is at a lower temperature than the surrounding air in the laboratory and an estimate has to be made for the heat gained from this source during its passage through the condenser. Furthermore, one end of the condenser box can 'see' the end of the boiler lagging and the heat absorbed from this source has also to be estimated. The correction is given by

$$\epsilon_c = (1/\mu)\,[(0{\cdot}25\,\mathrm{J\,s^{-1}\,degC^{-1}})\,(\theta_2-\theta_a)+(0{\cdot}033\,\mathrm{J\,s^{-1}\,degC^{-1}})\,(\theta_2-\theta_b)],$$

where ϵ_c = required correction to apparent enthalpy,
θ_a = ambient air temperature, and
θ_b = boiler lagging surface temperature.

The size of this correction is small, varying between −0·4 and +2·0 J/g.

In addition allowance must be made for the fact that all parts of the condenser may change in temperature during a run, thus either adding to or subtracting from the total amount of heat given up by the steam during a run. This correction ϵ_s has been evaluated in terms of the various water temperatures as approximately

$$\epsilon_s = (1/\mu\Delta t)\,(1000\,\mathrm{J\,degC^{-1}})\,[17\Delta\theta_1+60\Delta\theta_2+1{\cdot}5\Delta\theta_\mu],$$

where Δt = duration of experiment (seconds),
$\Delta\theta_1$ = rise in temperature of outgoing cooling water during run,
$\Delta\theta_2$ = rise in temperature of incoming cooling water during run, and
$\Delta\theta_\mu$ = rise in temperature of condensate during run.

The size of this correction is small, varying between ± 1 J/g.

(*d*) *Measurement of steam temperature and pressure*

The thermometer pocket (*D*, figure 1) and its connexion to the condenser are shown in detail in figure 3. The steam temperature is measured by a chromel-alumel sheathed thermocouple immersed axially in the pocket for about 11 in. with its junction close to the orifice. The couple is contained in a thin-walled stainless-steel sheath 0·125 in. in diameter and insulated from it by compressed magnesium oxide. The sheath is welded to a Nimonic plug which screws into the head of the pocket and the thermocouple junction is surrounded

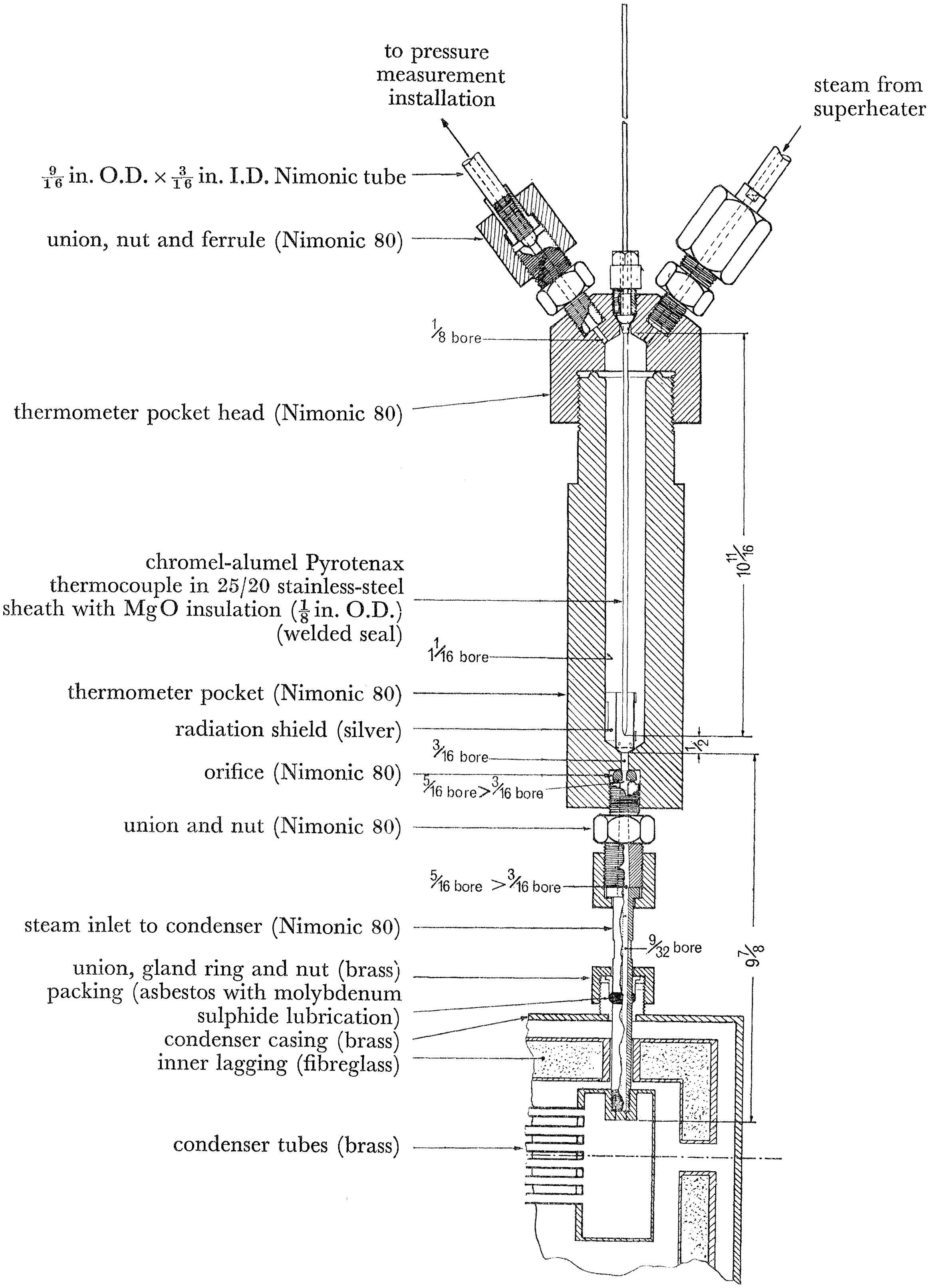

FIGURE 3. Thermometer pocket. (Dimensions in inches.)

by a silver radiation shield. The output of the couple is measured on a standard d.c. potentiometer using switched resistors and a slide wire. The reference potential is supplied by a Weston cell and the out-of-balance instrument is a micro-voltmeter.

The sheathed thermocouples are purchased from Pyrotenax Ltd in batches of seven, all cut from the same batch of wire. One of the seven is designated as the cold junction thermometer and the other six are calibrated with it at 50 degC intervals from 0 to 200 °C and at 100 degC intervals from 200 to 800 °C. All six were found to give identical results on calibration by the N. P.L. Periodically the thermocouple in use is checked by comparison with the standard platinum thermometer. In addition to the fixed point baths used, a Grace–Hall oil bath is used to obtain readings at precisely 50, 150 and 200 °C. The only variations found in use have been changes in the zero-point equivalent to a few hundredths of a degC.

The overall accuracy of the thermocouple readings is estimated to be $\pm 0{\cdot}25$ degC and it is believed that this is the error in the measurement of the steam temperature. The depth of immersion, 11 in., the small diameter of the wires, 0·03 in., and the thinness of the thermocouple sheath, 0·02 in., ensure that the conduction error is negligible. The diameter of the pocket is a compromise chosen to ensure turbulence of the steam flow under all experimental conditions and a velocity sufficiently small for the kinetic energy term in the energy balance to be negligible. The error caused by radiation exchange between the thermocouple, the radiation shield and the pocket wall is not calculable because the radiation absorption characteristics of steam are not known at the experimental conditions. However, the error would be negligible even in a transparent gas. From time to time extra thermocouples have been introduced into the pocket and it has been found that the recorded temperature does not vary axially by more than the estimated accuracy of measurement ($\pm 0{\cdot}25$ degC) over $\frac{1}{2}$ in. on either side of the measuring position.

There remain the errors due to the difficulty of reproducing exactly the International temperature scale fixed points. It is believed that at 400 °C (i.e. below the sulphur point), these errors are negligible but that at 700 °C they may be of the order of 0·5 degC.

The connexion to the pressure mercury installation is a 12 ft. tube which, at the end remote from the pocket, is cold and contains water. It is connected to a pressure vessel, *G* (figure 1) which contains a water-liquid paraffin interface and also makes connexion with a free-piston pressure balance, a Bourdon gauge and an oil injector. The position of the oil-water interface is located by treating the two fluids as the dielectric of a condenser, one plate of which is the wall of the vessel and the other an insulated probe in the centre. The variation in the capacitance of this condenser caused by movement of the oil-water interface is measured on a capacitance bridge.

The pressure balance used was similar to that described by Bett, Hayes & Newitt (1954), but without the mechanical rotating system and the constant temperature enclosure. It was calibrated against an assembly which had itself been calibrated against the primary pressure standard of Bett *et al.* The various hydrostatic heads in the system together amounted to approximately 10^{-3} bar, and are thus negligible. The overall accuracy of the pressure measurement is estimated to be $\pm 0{\cdot}5$ at 1000 bar and better than this at low pressures.

(*e*) *Flow measurement and the determination of the mass of condensate and of cooling water*

After leaving the condenser, the condensate passes by way of an after-cooler to a hinged vertical tube terminating in a fishtail orifice. At pre-determined intervals the hinged tube is made to swing through a small arc so that the issuing curtain of water cuts across a knife-edge and falls into a collecting tank F. After a fixed time interval it swings back and the contents of F are weighed. The switch which actuates the hinged tube simultaneously operates a similar device for the cooling water.

The time of collection is controlled from a synchronous clock which drives a gear train carrying cams which engage micro-switches, one of which completes a circuit causing a motor to move the hinged tube in one direction, while a second switch later reverses the motor and so turns the tube to its original position.

In the heat-loss correction, the rates of flow of cooling water and condensate appear as separate terms so that a knowledge of the accuracy of the time of collection is needed. Tests showed that the actual collecting time differed from the nominal collecting time by less than 0·2 s.

The mass of condensate is determined by means of a single-pan balance in which the load is balanced by the deflexion of a counterpoise arm. An optical system shows the movement of the arm on a ground-glass screen directly as a load in grammes.

The aluminium cans in which the condensate is collected have a capacity of 450 g and are fitted with screw tops. An after-cooler ensures that the condensate is only a few degrees above room temperature and the correction for evaporation is negligible. Experiments in which 100 weighings of random quantities of water were re-weighed on a standard balance, gave a standard deviation of ±0·047 g.

The cooling water is weighed on an equal-arm balance, which is poised to the nearest 100 g, the remainder of the load being read from a scale. The cans in which the cooling water is collected are of stainless steel or brass and have closely fitted covers of the same material; their capacity is approximately 8 kg of water. The balance is graduated to 0·5 g and read to 0·1 g. Experiments in which 100 random quantities of water were weighed, checked against the standard balance, gave a standard deviation of ±0·187 g. Both these balances and the sets of weights used were periodically checked against the standard balance accurate to 10 μg and reserved for standardizations, together with a set of weights of N.P.L. class 'A' standard of accuracy.

The cooling water is at a temperature of from 30 to 80 °C at the collecting point and some correction is necessary for the evaporation which occurs during collection. From the empirical corrections available, we chose that due to Hinchley (1922) who gives, for the evaporation from a free surface, the relation

$$\eta_M = (0{\cdot}95\,\mathrm{kg\,m^{-2}\,h^{-1}})\,At_M[(P_e-P_d)/50\,\mathrm{mmHg}]^{1{\cdot}2},$$

where
η_M = mass lost (kg),
A = evaporating surface,
t_M = time of collection,
P_e = water vapour pressure of cooling water, and
P_d = partial pressure of moisture in air.

This formula was checked by experiments in which water collections made in the usual way were compared with collections in a can specially designed to eliminate evaporation losses. A large number of experiments, made with a wide variety of water temperatures, air temperatures and humidities led to the conclusion that the form of Hinchley's relation correctly reflected the variations in condition, but that the numerical constant was low. The best representation of the evaporation was found to be

$$\eta_M = (1{\cdot}90\,\mathrm{kg\,m^{-2}\,h^{-1}})\,At_M[(P_\epsilon - P_d)/50\,\mathrm{mmHg}]^{1{\cdot}2}.$$

3. The experimental results

(a) *Computation of experimental results*

The major problems in all dynamic heat measurements arise from thermal lags, and it was therefore necessary to organize the computation of the results to show that the plant was steady: it was not sufficient simply to take the mean of the various readings, but their variation in time had also to be taken into account. This introduced difficulties with the platinum thermometer readings: the calculation of thermometer resistance required the knowledge of the Smith bridge readings in both 'A' and 'B' positions at the same time, which was impossible.

The method employed was to plot graphs of time against the two flow rates, the steam temperatures, the cooling water outlet thermometer resistance and any parameter which showed unusual trends. Any run in which any parameter showed abrupt changes, wide fluctuations or large changes with time was rejected and repeated. For the remainder, the evaporation correction was worked out, details of the thermometer and pressure gauge constants currently in use were added and the whole was sent to English Electric Co. Ltd, Data Processing Division, where it was fed into a DEUCE digital computer.

Within the computer, the reference numbers of the weights on the pressure balance were compared with the latest table of calibration of pressure balance weights, and converted to grammes. The interval between the first and last times at which all the parameters existed within the experiment was then divided into 31 equal subintervals. The converted pressure balance data, and all other data as received, were then subject to a second-order interpolation to bring them to the 32 subinterval bounds. At each of these 32 points the physical properties were produced from the instrument readings as follows:

Steam pressure

The load in grammes was multiplied by the value of gravitational acceleration at Imperial College ($981{\cdot}187\,\mathrm{cm/s^2}$), and divided by the effective cross-sectional area of the pressure balance piston to give the gauge pressure. The barometric pressure was then added and the absolute pressure obtained in bars.

Steam temperature

The readings were converted to temperature by using a polynomial derived from least-squares fitting of the latest thermocouple calibration figures.

Water temperatures and enthalpies

The cooling water inlet and outlet and condensate thermometer readings were all three handled in the same way. The resistance of the thermometer was obtained from

$$R_\theta = \tfrac{1}{2}[(A_0+B_0)-(A_1+B_1)],$$

where

R_θ = resistance of platinum thermometer,

A_0 = reading of variable resistance of Smith bridge with thermometer switched out and bridge in A position,

B_0 = reading of variable resistance of Smith bridge with thermometer switched out and bridge in B position,

A_1 = reading of variable resistance of Smith bridge with thermometer switched in and bridge in A position, and

B_1 = reading of variable resistance of Smith bridge with thermometer switched in and bridge in B position.

The resistance was converted to temperature by solving the equation

$$R_\theta = R_0\,(1+\alpha\theta+\beta\theta^2),$$

where R_0, α, and β were derived from the current calibration figures.

The temperature was then converted to enthalpy by a formula given by Le Fevre (1955). This states that the specific heat-capacity at constant pressure for water under a pressure of 1013250 dyn/cm^2 is C J g^{-1} degC^{-1}, where

$$\frac{C}{C_{15}} = \frac{4{\cdot}169\,036+3{\cdot}639\times10^{-14}(100+t)^{5{\cdot}26}+4{\cdot}67\times10^{-(2+0{\cdot}036t)}}{4{\cdot}169\,036+3{\cdot}639\times10^{-14}(100+15)^{5{\cdot}26}+4{\cdot}67\times10^{-(2+0{\cdot}54)}},$$

$$C_{15} = 4{\cdot}18546\,\mathrm{J\,g^{-1}\,degC^{-1}}, \quad \text{and} \quad t = \text{water temperature (°C)}.$$

This formula was produced by removing the premature rounding, and the errors of calculation or printing in the formula contained in the report of de Haas (1950) for the International Committee of Weights and Measures. The experimental observations supporting the formulation given in the report are those of Osborne, Stimson & Ginnings (1939*a*, *b*).

This formula is for the heat-capacity under a pressure of 1013250 dyn/cm^2, whilst the approved zero point for energy calculations on steam is the triple point, at which the internal energy of the liquid phase is to be taken as zero. To supplement the given formula the enthalpy of steam at 0 °C, 1013250 dyn/cm^2 pressure, namely 0·0600 J/g is needed.

Flow rates

The flow rates were obtained by adding the evaporation correction to the weight of cooling water and condensate and dividing by the time of collection specified.

Apparent enthalpy of steam

This was computed from the equation

$$H^*_{00} = (M/\mu)\,(h_1-h_2)+h_\mu.$$

The computer printed out values of H^*_{00}, P_0, T_0, M, μ, h_1, h_2 and h_μ at all 32 points and gave a summary consisting of the means of all the above values and their standard deviations.

An example of a typical experiment is shown in figures 4 and 5, and in tables 1 and 2. In table 1 is shown the data sent to DEUCE except for readings taken during the run. The latter are plotted against time, together with DEUCE's interpolations, in figure 4. In figure 5 the variation in physical properties as worked out by DEUCE are given and in table 2 is DEUCE's summary.

TABLE 1. AUXILIARY INPUT DATA TO DEUCE FOR ONE EXPERIMENT

*Block E*30, *run* 6
Orifice size: 0·011193 cm²

Steam thermocouple

ref. no. H. 6212 (2)

correlating equation: $T = -0{\cdot}057+253{\cdot}023\,(\tfrac{1}{10}E)-47{\cdot}522\,(\tfrac{1}{10}E)^2+100{\cdot}434\,(\tfrac{1}{10}E)^3-89{\cdot}681\,(\tfrac{1}{10}E)^4 +38{\cdot}537\,(\tfrac{1}{10}E)^5-8{\cdot}019\,(\tfrac{1}{10}E)^6+0{\cdot}652\,(\tfrac{1}{10}E)^7$

T in °C, E in mV.

Platinum thermometers

position	ref. no.	$R_0(\Omega)$	$10^3\alpha$	$10^7\beta$
cooling water inlet	079M	18·0616	3·9724	−5·892
cooling water outlet	078	17·9760	3·9695	−5·875
condensate	080	17·9617	3·9784	−5·874

Pressure balance

piston ref. no. K228
gauge pressure = (load in g × 3·0377 × 10⁻³) bar
atmospheric pressure = (barometer reading in mmHg × 1·333) bar

Weight table

wt. no.	mass (g)	wt. no.	mass (g)
161	6664·2	171	2665·5
162	6664·4	173	666·1
170	2665·9	177	133·3

Check list readings

	before	after
Smith bridge internal balance A position (Ω)	27·996	27·996
B position (Ω)	28·016	28·016
hygrometer: dry bulb temperature (°F)	80	80
wet bulb temperature (°F)	65	65·5
condensate temperature at fish tail (°C)	16·8	17·0
cooling water temperature at fish tail (°C)	55·3	55·4
barometric pressure (mmHg)	757	756

evaporation correction condensate nil
cooling water +0·81 g

TABLE 2. SUMMARY OF OUTPUT DATA FROM DEUCE FOR SAME EXPERIMENT

	units	mean	standard deviation
apparent enthalpy	J/g	3628·88	±2·49
pressure	bars	64·15	±0·04
temperature	°C	595·34	±0·18
condensate flow	g/s	7·305	±0·006
cooling water flow	g/s	131·055	±0·122
condensate enthalpy	J/g	287·71	±0·48
cooling water out enthalpy	J/g	233·74	±0·15
cooling water in enthalpy	J/g	47·49	+0·03

computation interval	103·5 s
duration of computed run	53 min.
duration of observations	61 min.

(*b*) *The energy balance*

The heat balance of the plant was

$$\mu(H-h_\mu) = M(h_1-h_2)+Q,$$

which may be written as

$$H = H^*+Q/\mu.$$

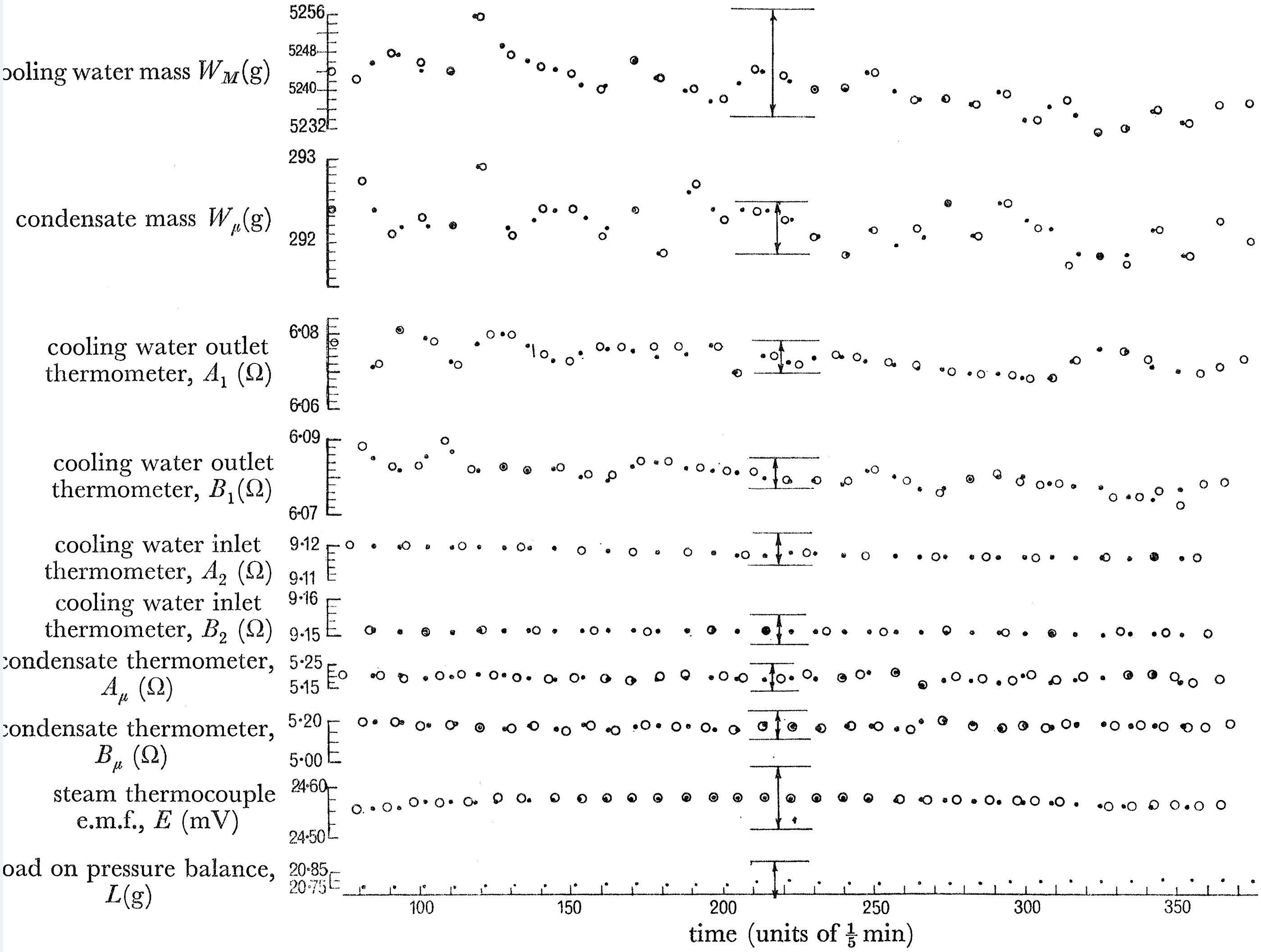

FIGURE 4. Input data from experiment and DEUCE's interpolations. The limits shown represent the variation of each parameter that will produce a change of one part in a thousand of the apparent enthalpy, assuming all the other parameters to remain constant, except for L, where the variation shown is that which will produce a change of one part in ten thousand of the apparent enthalpy. ○, experimental readings; ●, interpolations by DEUCE into experimental readings.

It will be seen that in the above equation the apparent enthalpy tends to the true enthalpy as the steam flow rate increases without limit, providing the heat leak remains finite. It will therefore be useful to consider the behaviour of each component of Q, as the steam flow rate increases.

If a fixed closed surface be drawn around the condenser, then Q is the sum of all the heat fluxes crossing the boundary, providing the boundary cuts the four points at which the temperature measurements are made. It is convenient to take as part of the boundary the surface of the lagging of the condenser and thermometer pocket (see figure 2): the boundary is closed at the thermometer pocket end by a plane at right angles to the steam thermocouple and passing through the thermocouple junction. The boundary at the exits from the condenser is drawn at the points where the cooling water inlet, cooling water outlet and condensate temperatures are measured, along the inside of their containing tubes, and across these tubes at right angles where they emerge from the condenser lagging.

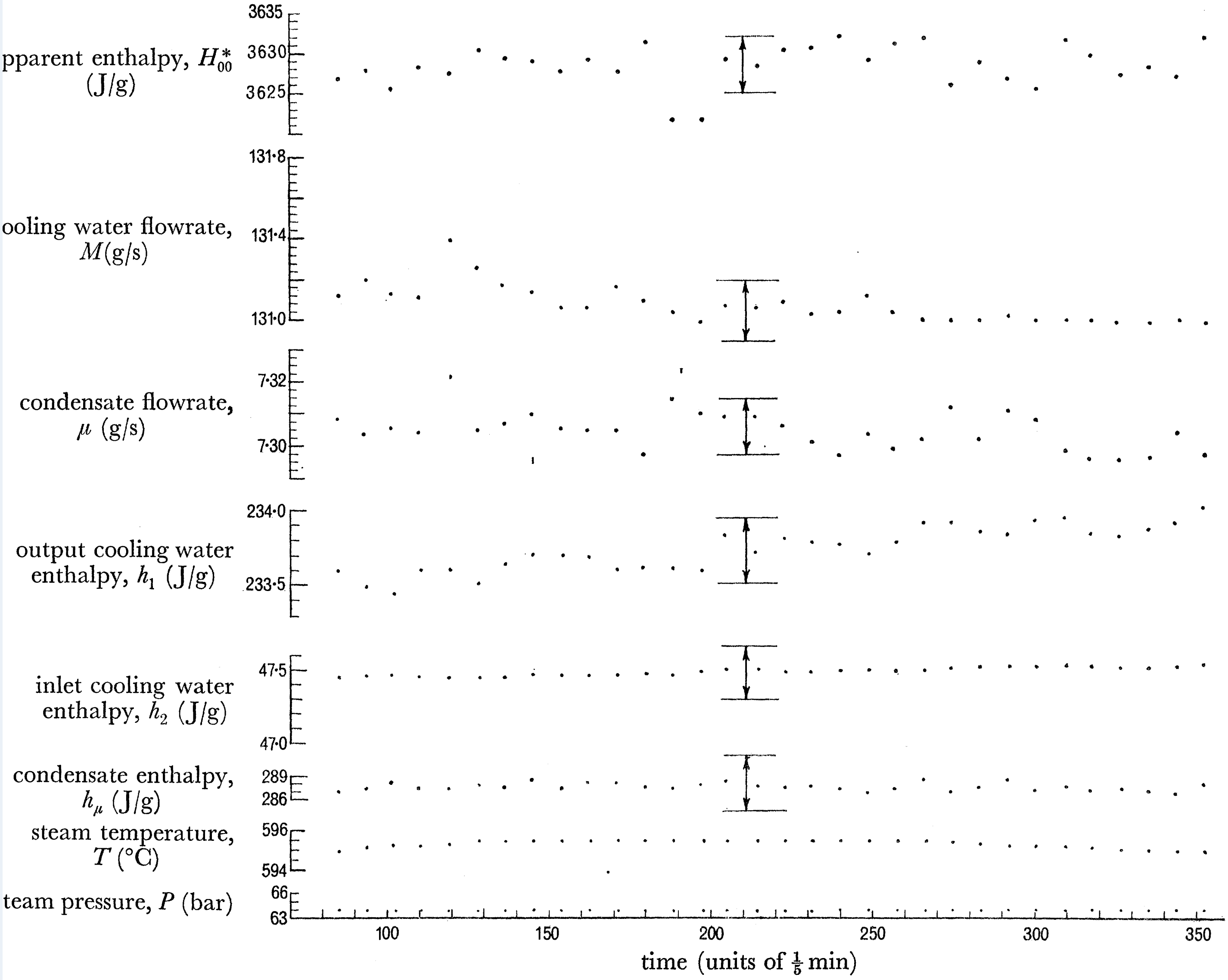

FIGURE 5. Output data from DEUCE. The limits shown represent the variation of each parameter that will produce a change of one part in a thousand of the apparent enthalpy, assuming all the other parameters to remain constant.

Before considering the boundary further, it is necessary to show that the use of the simplified heat balance in which the gravitational and kinetic energy terms are neglected, does not introduce a significant error.

The inlet and outlet of the steam flow through the boundary were at different heights and their differences could contribute a term of order of magnitude 3×10^{-3} J/g to the measured enthalpy. Similarly, the difference in heights of the inlet and outlet cooling water could contribute a maximum of $0{\cdot}7\times10^{-3}$ J/g. Both these terms are negligible.

The differences in kinetic energy of the steam passing the thermocouple junction and the condensate leaving the condenser depended partly on the density of the steam and hence the pressure and temperature of the experiment. Of the results reported, the kinetic energy difference was greatest at 60 bar, 700 °C, when it contributed $0{\cdot}5\times10^{-3}$ J/g to the enthalpy. The variation in kinetic energy of the cooling water entering and leaving the condenser contributed a term of between 10^{-3} and 10^{-4} J/g. These terms could also be neglected.

We may now return to a consideration of the heat fluxes crossing the boundary, beginning with the heat flux crossing that part of the boundary surface which is the surface of the lagging. The temperature differences determining this energy flux are $(T-\theta_A)$ and $(\theta_2-\theta_A)$. From the geometry of the apparatus, it would seem to be a reasonable assumption that the radiation and convection loss from the lagging around the condenser (as distinct from the lagging around the incoming steam pipe) is a function only of $(\theta_2-\theta_A)$. The energy flux under this assumption is $\mu\epsilon_c$, ϵ_c being the correction for the energy interchange between ambient air and condenser.

A net heat leak, q, may now be defined by

$$q = Q-\mu\epsilon_c.$$

The heat transfer across the remainder of the lagging (around the steam pipe entry to the condenser) is

$$K_1(\theta_S-\theta_a),$$

where

θ_S = temperature of surface of lagging

θ_a = temperature of ambient air, and

K_1 = a function incorporating the convection heat transfer coefficient, the equivalent radiant heat transfer coefficient and the area of the lagging.

The minimum value of this is zero when the surface temperature equals the ambient air temperature, and its maximum value is $K_1\,(T-\theta_a)$, since the temperature of the lagging can never rise above the steam temperature. Since K_1 is finite within these temperature limits, then, no matter how μ and M may vary, this part of q is finite and bounded.

To complete the consideration of the hot end of the boundary, there remains the heat conducted across the plane at right angles to the thermocouple. This may be written

$$\lambda_2 A_2\frac{\mathrm{d}\theta_M}{\mathrm{d}x}+\lambda_3 A_3\frac{\mathrm{d}\theta_L}{\mathrm{d}x},$$

where λ_2 = thermal conductivity of metal of thermometer pocket,

A_2 = area of pocket across which heat is conducted,

$\mathrm{d}\theta_M/\mathrm{d}x$ = temperature gradient in metal at boundary,

λ_3 = thermal conductivity of lagging around thermometer pocket,

A_3 = area of lagging across which heat is conducted, and

$\mathrm{d}\theta_L/\mathrm{d}x$ = temperature gradient in lagging at boundary.

The minimum value of this term is zero when the two temperature gradients are zero. The maximum numerical value is undetermined but is clearly finite: it cannot exceed that which would result if the steam at the end of its passage through the pocket were at its lowest possible temperature, which is the cooling water inlet temperature. Since λ_2 and λ_3 are finite within these temperature limits, then no matter how μ and M may vary, this part of q is finite and bounded.

At the cold end of the condenser, somewhat similar reasoning holds for the heat conducted across the boundary cutting the tubes carrying cooling water and condensate. There is for each tube a heat transfer of the form $\lambda_n A_n \,\mathrm{d}\theta/\mathrm{d}x$, where $n = 4, 5$ and 6, and in each case $\mathrm{d}\theta/\mathrm{d}x$, and hence the heat flux, remains finite no matter how μ and M vary.

The remaining parts of the boundary to be considered are those lying along the inner surfaces of the platinum thermometer pockets and the tubes carrying the water streams. The heat crossing these could have been directly measured by observing the temperature of the water where it leaves the lagging and comparing it with its temperature at the exit to the condenser. Provision was not made for this in design, and we hesitated to alter the plant after so many measurements had been made with it, lest we alter conditions significantly. However, it is sufficient to note that the heat transferred will depend on the temperature differences between the water and the tube and that these will remain finite no matter how μ and M will vary.

Thus the heat leak, q, is finite and bounded, and in the equation

$$H = H^* + q/\mu,$$

the apparent enthalpy does tend to the true enthalpy as the steam flow tends to infinity. A convenient method of procedure is therefore to perform experiments, at any fixed pressure and temperature, at various steam flows and from the results extrapolate to infinite steam flow, thus obtaining the true enthalpy. It can be said that, if the plant is run at a steady pressure and temperature, the difference between the apparent enthalpy and the true enthalpy will be due to various temperature gradients existing in the apparatus, and whatever these temperature gradients are, they will be determined by five factors only—the rate of flow of steam, the rate of flow of cooling water, the temperature of the incoming cooling water, the temperature of the surrounding atmosphere, and the material and dimensions of the plant. Since the last of these is unchanging and the effect of the ambient temperature is negligible within its possible variations, all the effects can be summed up in an expression which gives the true enthalpy as a function of the apparent enthalpy, the steam flow, the cooling water flow, and the cooling water inlet temperature.

Initial experiments showed that the temperature of the incoming cooling water did not effect the results within the range of variations of this parameter (approximately 5 to 25 °C). Therefore, at fixed steam pressures and temperatures a series of experiments were carried out in which the steam flow and cooling water flow rates were varied over as wide a range as possible within the limits of the plant, with the intention of fitting some equation of the form $H^* = f(\mu, M)$ to the results. First, however, two further corrections had to be made since the experiments could not be made at exactly the pressures and temperatures specified.

If the pressure and temperature of any experiment are P_0 and T_0 respectively instead of the nominal pressure and temperature, P_1 and T_1, at which a group of experiments are to be correlated, then the effect upon the enthalpy of the differences $(P_1 - P_0)$ and $(T_1 - T_0)$ must be taken into account before the correlation described in the previous section can be carried out.

The enthalpy at P_1 and T_1 is related to the enthalpy at P_0 and T_0 by

$$H_1 = H_0 + \left(\frac{\partial H}{\partial P}\right)_T \Delta P + \left(\frac{\partial H}{\partial T}\right)_P \Delta T,$$

providing higher order terms of the form $\frac{1}{2}(\partial^2 H/\partial^2 P)_T \Delta P^2$, etc., may be neglected. But

$$H_0 = H^*_{00} + q/\mu,$$

and so

$$H_1 = H^*_{00} + (\partial H/\partial P)_T \Delta P + (\partial H/\partial T)_P \Delta T + q/\mu.$$

Values of $(\partial H/\partial T)_P$ were, with the exception to be noted, taken from the tables produced by Sirota *et al.* (1963 *a*) for consideration at the 1963 International Conference on the Properties of Steam. These tables are based on the experimental work of Sirota and of Koch, and are in agreement with the '1963 International skeleton tables.'

No experimental values of $(\partial H/\partial P)_T$ are available in our experimental range and estimates of it were therefore made by the differencing of several steam tables and the graphical smoothing of each set of differences. The mean of the several results were taken as the best value of $(\partial H/\partial P)_T$.

The values used are given in table 3. The corrected enthalpy values finally used for correlation are thus

$$(H^*_{00} + \epsilon_c + \epsilon_s + (\partial H/\partial P)_T \Delta P + (\partial H/\partial T)_P \Delta T),$$

which are given the symbol H^*_{11}.

TABLE 3. VALUES OF $(\partial H/\partial T)_P$ AND $(\partial H/\partial P)_T$ USED FOR CORRECTION OF RESULTS

	T (°C)		
P (bar)	400	600	700
	$(\partial H/\partial T)_P$ (J g^{-1} degC^{-1})		
60	2·466	2·324	2·345
200	6·460	2·776	2·608
400	8·792	3·622	3·027
600	6·012	4·526	3·479
800	5·380	5·024	3·873
	$(\partial H/\partial P)_T$ (J g^{-1} bar^{-1})		
60	−2·204	−1·036	−0·769
200	−3·842	−0·857	−0·719
400	−0·995	−0·904	−0·620
600	−0·235	−0·913	−0·575
800	−0·123	−0·670	−0·492

Summing up, there is available, at a pressure P_1 and temperature T_1, a number of corrected enthalpies, H^*_{11}, for a range of values of μ and M. These are to be correlated in the form

$$H_1 = H^*_{11} + q/\mu,$$

subject to the conditions that for all μ and all M, q remains finite.

Without further knowledge of the system, the relation between q, M and μ is arbitrary, subject to the conditions stated, and a simple function which meets these conditions is

$$q = \sum_{r=0}^{R} \sum_{n=0}^{N} a_{rn} \mu^{-r} M^{-n}.$$

Introducing for convenience the symbols $\alpha = \mu^{-1}$ and $\omega = M^{-1}$, we have

$$H_{11}^{*} = H_1 + \alpha \left[\sum_{r=0}^{R} \sum_{n=0}^{N} a_{rn} \alpha^r \omega^n \right].$$

The experimental results were fitted by least-squares methods to some of the simpler equations generated by the above function on the DEUCE computer of the National Engineering Laboratory. The goodness of fit of each equation was compared with the others by comparing the ratio of the sum of the squares of the residuals with the value of the F-distribution at the appropriate number of degrees of freedom. By fixing the conditions that the improvement in fit caused by adding an extra term to any equation should be significant at the 5% level, two equations out of twenty-four investigated were selected. The equation with two disposal constants which best fitted the results was

$$H_{11}^{*} = a_1 + a_2 \alpha,$$

the equation with three disposable constants which best fitted the results was

$$H_{11}^{*} = a_1 + a_2 \alpha + a_3 \alpha \omega,$$

and no increase in the number of disposable constants significantly improved the fit. The values of the enthalpy, $(= a_1)$, given by the two selected equations were in every case within 1 J/g of each other, but in every case the goodness of fit of the two-constant equation was significantly worse than that of the three-constant equation, so the latter has been used, with the single exception to be noted.

A modification of this procedure was then investigated. The regression equation was written as

$$(H_{00}^{*} + \epsilon_c + \epsilon_s) = a_1 + a_2 \alpha + a_3 \alpha \omega + a_4 \Delta P + a_5 \Delta T,$$

and the least-squares fit to the experimental results gave, in addition to the enthalpy and the heat leak, values of $(\partial H/\partial P)_T (= a_4)$ and $(\partial H/\partial T)_P (= a_5)$.

In every case the value of the enthalpy obtained was within one standard deviation of the result obtained from the three-constant equation, but the values of $(\partial H/\partial T)_P$ were accompanied by coefficients of variation of the order of 5 to 50%, and the values of $(\partial H/\partial P)_T$ by coefficients of variation of the order of 10 to 100%. This equation was therefore only retained for use with the 1000 bar, 400 °C results, where no estimates of $(\partial H/\partial P)_T$ or $(\partial H/\partial T)_P$ were available, except by extrapolation.

(c) *Errors*

In the experiments carried out at any one pressure and temperature, the enthalpies are calculated at three successive removes from the original pointer readings and it will be convenient to consider the errors at each of the following levels.

(i) *Apparent enthalpy points* (H_K^{*})

The 32 apparent enthalpies calculated for each run by DEUCE at equal intervals of time, usually from 32 sets of pointer-readings originally at random intervals of time.

(ii) *Apparent enthalpy results* (H^*_{00})

The mean of the 32 apparent enthalpy points calculated for each run.

(iii) *Enthalpy* (H_1)

The result obtained by a least-squares correlation of all the apparent enthalpy results, after correcting them by ϵ_s and ϵ_c and for deviations in pressure and temperature from those required.

Apparent enthalpy points (H^*_K). When all the precautions and corrections that suggest themselves have been taken, the errors remaining in the apparent enthalpy points are the normally distributed errors due to instruments and operators and the errors due to the interpolations.

The errors of interpolation are very small compared to the other errors, and thus can be neglected, but the fact that interpolations have been made increases the problem of finding the true error associated with each point, since each interpolated value depends on several instrument readings. The effect of this on the true error has been reduced in general, by making 32 readings into which 32 interpolations are made, and can be further reduced by using for further computation, not each individual point, but a statistic comprising all 32. Since this is what is done the DEUCE interpolations will here be treated as though they were actual pointer readings.

If

$$X = f(x_1, x_2, x_3, \ldots, x_n),$$

where x_1, x_2, etc., are measurements which vary independently, then

$$V(X) = \left(\frac{\partial X}{\partial x_1}\right)^2 V(x_1) + \left(\frac{\partial X}{\partial x_2}\right)^2 V(x_2) + \ldots + \left(\frac{\partial X}{\partial x_n}\right)^2 V(x_n),$$

where $V(x_n)$ is the variance of x_n.

As many as possible of the instruments used have had their variances measured by independent experiments which have been discussed. Collecting them together:

$$\begin{aligned}
\sigma(W_M) &= 0{\cdot}187\,\text{g}, & V(W_M) &= 350\times10^{-4}\,\text{g}^2,\\
\sigma(\eta_M) &= 0{\cdot}05\,\text{g}, & V(\eta_M) &= 25\times10^{-4}\,\text{g}^2,\\
\sigma(W_\mu) &= 0{\cdot}047\,\text{g}, & V(W_\mu) &= 22\times10^{-4}\,\text{g}^2,\\
\sigma(\theta_1) &= 0{\cdot}007\,\text{degC}, & V(\theta_1) &= 0{\cdot}74\times10^{-4}\,(\text{degC})^2,\\
\sigma(\theta_2) &= 0{\cdot}004\,\text{degC}, & V(\theta_2) &= 0{\cdot}16\times10^{-4}\,(\text{degC})^2,\\
\sigma(\theta_\mu) &= 0{\cdot}034\,\text{degC}, & V(\theta_\mu) &= 11{\cdot}5\times10^{-4}\,(\text{degC})^2,
\end{aligned}$$

where $\sigma(x_n)$ is the standard deviation of x_n.

The values for $V(t_\mu)$ and $V(t_M)$ are more difficult to define: our experiments only showed a variation equal to the accuracy of the method of checking, i.e. the true error was probably less than this. Without further evidence, it would seem to be reasonable to assume that this variation represents the range of values possible. Bearing in mind that, the range, R, of a statistic is approximately three times its standard deviation, we have

$$R(t_M) = R(t_\mu) = \pm 0{\cdot}02\,\text{s},$$

$$\sigma(t) = \pm 0{\cdot}007\,\text{s}, \qquad V(t) = 0{\cdot}49\times10^{-4}\,\text{s}^2.$$

If the equation

$$H^*_{00} = (M/\mu)\,(h_1-h_2)+h_\mu$$

is now rewritten in terms of the variables measured

$$H^*_K = \frac{W_M+\eta_M}{t_M}\,\frac{t_\mu}{W_\mu}\times 4{\cdot}19\,(\theta_1-\theta_2)-4{\cdot}19\,\theta_\mu,$$

using the approximate relation $h_x = 4{\cdot}19\theta_x$ and using H^*_K as the symbol for one apparent enthalpy point, this equation becomes, as an error equation

$$V(H^*_K) = (H^*_K-h_\mu)^2\left[\frac{V(W_M)+V(\eta_M)}{(W_M+\eta_M)^2}+\frac{V(W_\mu)}{W^2_\mu}+\frac{V(t_M)}{t^2_M}+\frac{V(t_\mu)}{t^2_\mu}\right]$$
$$+4{\cdot}19^2\frac{M^2}{\mu^2}\,[V(\theta_1)+V(\theta_2)]+4{\cdot}19^2\,V(\theta_\mu);$$

putting in values and noting that $t_M \simeq t_\mu$, we have

$$10^4\,V(H^*_K) = \left(\frac{H^*_K-h_\mu}{t_\mu}\right)^2\left[\frac{375\,\mathrm{g}^2}{M^2}+\frac{22\mathrm{g}^2}{\mu^2}+1\mathrm{s}^2\right]+\left[11{\cdot}1\,\frac{M^2}{\mu^2}+201\right]\frac{\mathrm{J}^2}{\mathrm{g}^2}.$$

The value of $V(H^*_K)$ resulting from this equation proves to be constant for all variations of the quantities on the right-hand side of the equation found during any given run. Hence no difference is caused by using the interpolated values instead of the original pointer readings.

Apparent enthalpy results (H^*_{00}). These results are the mean of the 32 points obtained during a run, the errors of which have been discussed above. The error of this mean must be affected not only by the errors of each point due to instrument readings, but also by real fluctuations of the plant during the run. Allowance must be made for these fluctuations and it can be shown that

$$V(H^*_{00}) = V(f)+(1/n)\,\Sigma\,V(H^*_K),$$

where

$V(H^*_{00})$ = variance of apparent enthalpy result,
$V(H^*_K)$ = variance of apparent enthalpy point,
$V(f)$ = variance of fluctuations of H^* due to plant, and
n = number of apparent enthalpy points in one apparent enthalpy result.

In any experiment, the values of $V(H^*_K)$ are uniform, and the standard deviation of H^*_{00} given in the DEUCE summary includes both the errors due to fluctuations and those due to instrument errors. Thus there is no need to evaluate $V(H^*_K)$ in every case. As an example, however, table 4 has been included, which breaks down the errors of the apparent enthalpy of all 60 bar, 600 °C results into their component parts.

The errors in T and P can be considered in the same way. The corrections ϵ_c and ϵ_s are approximate theoretical calculations, the errors of which are not known but their magnitude is so small that the errors propagated may be regarded as negligible.

Formally, however, we have from the equation

$$H^*_{11} = H^*_{00}+(\partial H/\partial T)_P\Delta T+(\partial H/\partial P)_T\Delta P+\epsilon_c+\epsilon_s,$$

the error equation

$$V(H^*_{11}) = V(H^*_{00}) + (\partial H/\partial T)^2_P\, V(T_0) + (\partial H/\partial P)^2_T\, V(P_0) + (T_1 - T_0)^2\, V(\partial H/\partial T)_P$$
$$+ (P_1 - P_0)^2\, V(\partial H/\partial P)_T + V(\epsilon_c) + V(\epsilon_s)$$

as the error equation for H^*_{11} corresponding to that for H^*_{00}.

TABLE 4. DETAILS OF THE ERRORS IN THE APPARENT SPECIFIC ENTHALPY OF EXPERIMENTS CARRIED OUT AT 60 BAR, 600 °C

	variances ((J/g)^2)								standard deviations (J/g)		
	due to instrument and observation errors of						due to fluctuations		due to		
experiment ref. no.	M	μ	t	h_1+h_2	h_s	total		total	instruments	fluctuations	total
E 30. 1	0·03	0·52	1·24	1·38	0·25	3·42	70·02	73·44	1·8	8·4	8·6
2	0·02	0·28	0·69	1·32	0·25	2·56	43·41	45·97	1·6	6·6	6·8
4	0·02	0·29	0·70	1·44	0·25	2·70	7·73	10·43	1·6	2·8	3·2
5	0·02	0·52	1·27	2·82	0·25	4·88	12·09	16·97	2·2	3·5	4·1
6	0·02	0·29	0·70	1·61	0·25	2·87	3·33	6·20	1·7	1·8	2·5
7	0·02	0·28	0·70	1·09	0·25	2·34	14·72	17·06	1·5	3·8	4·1
8	0·03	0·38	0·70	0·80	0·25	2·16	17·29	19·45	1·5	4·2	4·4
10	0·02	0·35	0·70	1·44	0·25	2·76	8·00	10·76	1·7	2·8	3·3
12	0·02	0·64	1·29	2·76	0·25	4·96	18·37	23·33	2·2	4·3	4·8
13	0·02	0·63	1·29	3·62	0·25	5·81	39·48	45·29	2·4	6·3	6·7
14	0·03	0·34	0·69	1·09	0·25	2·40	15·66	18·06	1·6	4·0	4·2
15	0·04	0·35	0·68	0·80	0·25	2·12	36·44	38·56	1·5	6·0	6·2
17	0·02	0·67	1·28	2·88	0·25	5·10	17·56	22·66	2·3	4·2	4·8
E 31. 8	0·01	0·82	0·32	5·35	0·25	6·75	44·52	51·27	2·6	6·7	7·2
13	0·01	3·49	1·35	20·47	0·25	25·57	148·14	173·71	5·1	12·2	13·2
14	0·02	1·88	0·74	8·57	0·25	11·46	65·10	76·56	3·4	8·1	8·8
16	0·02	0·81	0·32	3·91	0·25	5·31	33·88	39·19	2·3	5·8	6·3
E 30. 19	0·02	0·36	0·70	1·67	0·25	3·00	8·42	11·42	1·7	2·9	3·4
E 32. 13	0·02	1·10	0·73	4·83	0·25	6·93	84·85	91·78	2·6	9·2	9·6
14	0·02	0·48	0·32	2·59	0·25	3·66	28·15	31·81	1·9	5·3	5·6
16	0·02	0·47	0·32	2·07	0·25	3·13	38·21	41·34	1·8	6·2	6·4
18	0·02	1·98	1·32	8·16	0·25	11·73	123·53	135·26	3·4	11·1	11·6
21	0·01	0·48	0·32	3·34	0·25	4·40	39·96	44·36	2·1	6·3	6·7
E 33. 11	0·02	0·29	0·31	1·15	0·25	2·02	23·18	25·20	1·4	4·8	5·0
12	0·02	1·14	1·30	4·14	0·25	6·85	324·03	330·88	2·6	18·0	18·2
13	0·02	0·27	0·31	1·21	0·25	2·06	14·34	16·40	1·4	3·8	4·0
14	0·02	0·63	0·72	2·36	0·25	3·98	29·78	33·76	2·0	5·5	5·8
15	0·04	0·62	0·71	1·50	0·25	3·12	29·94	33·06	1·8	5·5	5·8
16	0·02	0·27	0·31	0·98	0·25	1·83	15·73	17·56	1·4	4·0	4·2
19	0·02	0·27	0·31	1·26	0·25	2·11	21·61	23·72	1·5	4·6	4·9

Enthalpy result (H_1). The corrected apparent enthalpy results, H^*_{11}, are correlated to give the enthalpy by

$$H^*_{11} = H_1 + a_2\alpha + a_3\alpha\omega$$

by least-squares fitting, and this statistical process itself introduces errors. It can be shown that the error in H_1, i.e. the error in the intercept, is given by

$$V(H_1) = S^2\left[\frac{1}{n} + \frac{\Sigma(A-\bar{\alpha})^2}{\Sigma(\alpha-\bar{\alpha})^2} + \frac{\Sigma(A\Omega-\overline{\alpha\omega})^2}{\Sigma(\alpha\omega-\overline{\alpha\omega})^2}\right],$$

where $A = 0$, $\Omega = 0$, $n =$ number of experimental points (H^*_{11}), and

$$S^2 = \frac{1}{n-3}[\Sigma(H^*_{11}-\overline{H^*_{11}})^2 - a_2\,\Sigma\,(H^*_{11}-\overline{H^*_{11}})\,(\alpha-\overline{\alpha}) - a_3\,\Sigma(H^*_{11}-\overline{H^*_{11}})\,(\alpha\omega-\overline{\alpha\omega})].$$

On inspection, it will be seen that this equation takes account of the range of α and $\alpha\omega$ over which experiments were performed, the amount of extrapolation of α and $\alpha\omega$ needed to find the intercept, the correlation between H^*_{11} and α and between H^*_{11} and $\alpha\omega$, and the number of experiments performed. In addition, it also allows for the variance of H^*_{11}, since

$$nV(H^*_{11}) = \Sigma(H^*_{11}-\overline{H^*_{11}})^2$$

and

$$nV(H^*_{11}) \simeq V_1(H^*_{11}) + V_2(H^*_{11}) + V_3(H^*_{11}) + \ldots + V_n(H^*_{11}),$$

where $V_r\ (H^*_{11})$ is the variance of any one corrected apparent enthalpy (the assumption of homoscedasticity).

Thus the value of $V(H_1)$ resulting from the least squares fitting of the selected equation sums up all the errors of surface fitting, and includes a term which takes account of the errors of the individual H^*_{11}. It has been shown that the error of H^*_{11} includes errors due to corrections and to H^*_{00} and further that the error of H^*_{00} includes the variations caused by fluctuations of the plant and the errors of observation of the original readings. The standard deviation $\sigma(H_1)$ is therefore the figure quoted in table 5 as the error of our results.

TABLE 5. EXPERIMENTAL VALUES FOR THE SPECIFIC ENTHALPY OF STEAM

H and σH in J/g

	T (°C)								
	400			600			700		
P (bar)	H	σH	n	H	σH	n	H	σH	n
60	3179·9	1·3	30	3656·1	1·2	30	3896·1	3·7	30
200	2817·3	2·5	37	3539·1	1·2	31	3804·2	1·8	16
400	1927·7	2·5	20	3343·6	2·0	16	3676·8	3·7	15
600	1846·1	3·6	17	3150·7	2·3	23	3557·2	5·0	22
800	1811·7	5·0	35	2978·1	3·5	17	3430·6	4·2	25
1000	1804·7	2·9	18						

n = no. of experiments.

(*d*) *Results*

The experiments reported here were performed between October 1959 and May 1964, and consist of 382 results, each the mean of about thirty complete sets of readings, from which seventeen enthalpy values have been found. These seventeen values are given in table 5, together with their standard deviation, and the number of experiments made at each steam condition. Extended tables, showing the results of each of the 382 experiments, are given in our reports to E.R.A. (Newitt, Angus & Hooper 1964*a*) and to C.E.G.B. (Newitt, Angus & Hooper 1964*b*).

In table 6 our results are compared with those of other workers and with the figures given in the '1963 International skeleton tables'. In some cases small interpolations had to be made to bring the values to the same conditions of pressure and temperature.

Comparison with the work of Callendar & Egerton (1960) is possible at four steam conditions. Their error is stated to be about 2 J/g, and in the light of this, the only significant difference between their work and the present results is at 200 bar, 600 °C, where it is 7·3 J/g. It must be borne in mind that their estimate of error is an average figure for all their experiments, while 200 bar and 600 °C represent the extreme limit of their plant at which experiments were made only with difficulty.

Table 6. Comparison of results with those of other determinations and with the 1963 International skeleton table

Entries in body of table in J/g

		Angus & Newitt result minus						
T (°C)	P (bar)	Callendar & Egerton	Havliček & Miškovský	Vukalovich *et al.*	Blank *et al.*	Sirota *et al.*	1963 I.S.T.	tolerance
400	60	+2·9	+4·9	—	—	−1·2	+2	4
	200	+4·0	+1·5	+4·0	—	—	−2	8
	400	—	−6·4	—	—	−2·3	−6	8
	600	—	—	—	—	+2·9	−1	8
	800	—	—	—	—	—	−2	8
	1000	—	—	—	—	—	+9	8
600	60	−0·2	—	—	—	—	−2	6
	200	+7·3	—	+7·9	−0·4	—	+1	10
	400	—	—	+1·2	−11·4	−3·5	−3	10
	600	—	—	—	—	−4·3	−2	10
	800	—	—	—	—	—	−5	10
700	60	—	—	—	—	—	+4	8
	200	—	—	—	—	—	−1	11
	400	—	—	—	—	—	+1	13
	600	—	—	—	—	—	+10	13
	800	—	—	—	—	—	+2	13

Comparison with Havliček & Miškovský (1936) is possible at three conditions, and in each case the difference from the present results is less than their stated experimental error of about 7 J/g. Both the above installations were similar to the present one, but that of Vukalovich, Zubarev & Prusakov (1958, 1962) differed significantly in that the steam flow was divided into two unequal parts through duplicate calorimeters and measuring systems, thus, in principle, making it possible to measure the heat leak correction with one experiment, although, in practice, small corrections are still needed. Comparison with their work is possible at three steam conditions: their experimental error is given as about 6 J/g and only at 200 bar, 600 °C does the difference, 7·9 J/g, exceed the combined errors of the two experiments.

Blank, Schmidt & Schmidt (1962) used a completely different method of measurement, measuring the temperature rise caused by a measured input of electrical energy. By working along isobars and summing their results they were able to produce values of total enthalpy, providing a base value was given at the lowest temperature. Only two points are available for comparison. Their values were obtained by adding to the experimental results a base value obtained from an extension of Koch's equation of state, as used in the sixth (1963) edition of the VDI steam tables. These differ from the values obtained by interpolation in the '1963 International skeleton tables' and if these latter values are used, the differences of −0·4 and −11·4 J/g become −4·7 and +8·1 J/g respectively.

Comparisons are also included with the enthalpy calculated by Sirota *et al.* from their specific heat measurements (1956, 1958, 1959, 1960, 1962*a*, *b*, 1963*a*, *b*). These comparisons can be made at five steam conditions and in every case the difference is negligible.

Comparisons are also shown with the appropriate entry from the '1963 International skeleton tables', and the relevant tolerance is given. In assessing this part of the table it is necessary to note that in preparing this skeleton, the International Commission on the Properties of Steam had available to them the present results at 60, 200 and 400 bar on the 400 °C isotherm, at 60, 200 and 400 bar at 600 °C and at 60 and 200 bar at 700 °C. They also had available Sirota's results up to 500 bar and all the results of Callendar & Egerton and Havliček & Miškovksý.

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