dioxide such as the upper limb of the mercury separator. Variations in the temperature of this volume of gas will not only disturb the phase equilibrium itself, but may also adversely affect the precision of estimation of the equilibrium load on the pressure balance by causing movements in the pressure transmitting fluid. The ambient temperature in the measurement room was maintained to within about $\pm 0\cdot 5$ degc, from a mean value of $21\cdot 5°$c, during the relevant periods. Due, however, to the massive construction of the mercury separator combined with thermal lagging, the corresponding variations in the temperature of this unit were only about $\pm 0\cdot 05$ degc. These variations were very slow and there was no evidence that their effects, during the relatively short periods required for the definitive measurements, were a source of appreciable uncertainty.

2.3. *Pressure measurement*

The pressure measurements were carried out by direct use of the Laboratory's standard pressure balances, calibrated by procedures developed at the National Physical Laboratory (Dadson 1955, 1958, Dadson, Greig and Horner 1965). To ensure optimum sensitivity the balances were used with the piston and load system freely rotating. In order to minimize variations in the volume of the system due to vertical movements of the piston the normal range of this movement was reduced to about $0\cdot 25$ mm. Observations of piston level were made using optical projection with a magnification of some 35 : 1 and with this arrangement it was possible to determine the balance load at equilibrium to within 1 part in 10^5.

As already mentioned, and indicated in the figure, the pressure balance (No. 1) used for the vapour pressure observations was so arranged that the pressure transmitting fluid, in this case oil, was separated from the carbon dioxide system by a mercury U-tube separator. This arrangement was chosen in order to avoid undesirable effects caused by prolonged contact between the compressed carbon dioxide and oil, such as instability due to the tendency for the gas to go into solution, and the risk of contamination of the equilibrium cell by oil vapour. Each group of pressure measurements must be corrected for the hydrostatic head between the reference level of the balance and that of the gas–liquid interface in the vapour pressure cell, and this quantity is best determined by direct measurement. For this purpose another similar pressure balance (No. 2) was connected temporarily to the gas limb of the mercury separator with the gas–oil interface located, as indicated in the figure, at the same level as the centre of the vapour pressure cell. Balances 1 and 2 were then balanced against one another with the mercury level indicator set to the same reading as in the actual vapour pressure measurements. The difference between the two equilibrating loads, with allowance for the effective areas and known auxiliary effects, then determined the hydrostatic head correction. As this latter measurement was of very brief duration the risk of contamination effects was inappreciable.

In a subsidiary series of tests the effect of periodically breaking the liquid surface of the carbon dioxide was investigated, using the magnetic stirrer, but this was found to have no measureable effect on the resultant vapour pressure.

2.4. *Observational procedure*

To prepare the system, the pressure circuit was first chemically cleaned and then evacuated for several hours to a final pressure of the order of 10^{-5} bar, using a two-stage rotary pump. During this period the piping and associated fittings were heated to a temperature of roughly $300°$c with the thermal insulation temporarily removed. The pressure vessel was then immersed in ice at $0°$c for a period of about 1 hour during which it was filled by condensation with pure carbon dioxide which was admitted to the system at a pressure of about 60 bars.

The pressure vessel was then transferred to the triple point cell and the valve in the line from the carbon dioxide supply closed. Gas was then released from the system until the pressure was about 1% higher than the vapour pressure at $0\cdot 01°$c, and a period of about 1 hour allowed for the system to recover from the disturbances caused by the filling process. The pressure was then rapidly released to a value about $0\cdot 05\%$ *below* the vapour pressure

and a further period of some 30 minutes allowed for evaporation from the carbon dioxide in the pressure vessel to establish the correct vapour pressure. This was then measured with the pressure balance, at intervals, until a final value was reached, indicating full recovery of equilibrium.

The pressure was then again released to a value about 0.05% below the vapour pressure, and the above procedure repeated. This process was continued while an adequate supply of condensed carbon dioxide remained in the pressure vessel. The system was then prepared again in readiness for the next series of measurements.

3. Results

3.1. *Mean value, dispersion and estimation of error*

The mean value of the final group of 29 separate determinations, corresponding to the temperature $0.0100°C$, is given below in SI units together with some equivalents in common use:

SI units	$3.485\ 64$ MN m^{-2}
bar scale	$34.856\ 4$ bars
international atmospheres	$34.400\ 6$ atm
conventional barometric millimetres of mercury	$26\ 144.5$ mmHg

The standard deviation of the group was $0.000\ 17$ MN m^{-2}, giving a confidence interval of $\pm 0.000\ 065$ MN m^{-2} from the mean for a probability of 95%. The median value, $3.485\ 63$ MN m^{-2}, was virtually indistinguishable from the mean.

The principal *systematic* error is due to the uncertainty in the effective area of the piston–cylinder assembly of pressure balance No. 1, which, in the pressure region concerned, is known to within 1 part in 10^5. The associated uncertainty in the measured vapour pressure is therefore within $\pm 0.000\ 035$ MN m^{-2}. It is estimated that the remaining systematic errors associated with measurements of the hydrostatic head correction and the barometric pressure, and uncertainties in the local value of gravity and the exact temperature of the triple point cell, should not exceed a further $\pm 0.000\ 02$ MN m^{-2}. The total systematic error may therefore be taken to be within the limits $\pm 0.000\ 055$ MN m^{-2}.

The observed dispersion no doubt arose from a combination of several small effects, including minor departures from temperature uniformity, random errors in the estimation of the load on the pressure balance and in the barometric pressure, and in the identification of the mercury level in the upper limb of the mercury separator. Of these, uncertainty in the mercury level arising from capillarity effects, with the possibility of random errors of, say, ± 0.5 mm, may have made the largest contribution.

On this basis the total uncertainty associated with the mean value given above, corresponding to a confidence level of 95%, is within $\pm 0.000\ 12$ MN m^{-2}.

3.2. *Comparison with former results*

For convenient reference the results of the three former investigations considered are summarized, together with our present results, in the table.

We first consider the investigations of Bridgeman (1927) at the Massachusetts Institute of Technology, and of Meyers and Van Dusen (1933) at the National Bureau of Standards, Washington. Work prior to 1927 has been adequately reviewed by Meyers and Van Dusen.

Bridgeman set out to measure the vapour pressure at $0°C$ to the best available accuracy, with the specific intention of establishing a fixed calibration point. Four pressure balances, calibrated by reference to a 9-metre mercury manometer were used. The final series of 30 measurements gave the average value $26\ 144.7$ mmHg with which were associated limits of accuracy of ± 1 mmHg. A detailed study of the data indicates, however, that systematic errors considerably higher than these limits may have been present. For example, the results obtained with two of the pressure balances—designated D8L and D8S—show a systematic difference of about 3 mmHg on the same sample of carbon dioxide, and a similar effect is present in a preliminary set of data (see table 1 of Bridgeman's paper) which were