Summary of experimental values†

Date	Authors	Vapour pressure at 0°C			Vapour pressure at 0·01°C		
		MN m^{-2}	atm	mmHg	MN m^{-2}	atm	mmHg
1927	Bridgeman	3·485 66	34·4009	26 144·7	(3·486 58)	(34·4100)	(26 151·6)
1933	Meyers and Van Dusen	3·484 96	34·3939	26 139·5	(3·485 88)	(34·4030)	(26 146·4)
1950	Michels et al.	(3·484 67)	(34·3910)	(26 137·2)	3·485 59	34·4001	26 144·1
1966	This paper	(3·484 72)	(34·3915)	(26 137·6)	3·485 64	34·4006	26 144·5

† Values shown in brackets for 0°C are deduced from the actual experimental values at 0·01°C, and vice versa, using the known rate of change of vapour pressure, 0·91 atm degc^{-1}, in the neighbourhood of 0°C.

not used in deriving the final results.   Again, the pair of balances D8L and D9S were used with two samples of carbon dioxide and showed substantially the same systematic difference —about 2 mmHg—in each case.   The existence, quite apart from random dispersion, of systematic effects of this magnitude is difficult to reconcile with a final estimate of error of only ±1 mmHg, especially as the *differences* referred to may not necessarily reveal the *total* systematic error involved.

The comparable measurements of Meyers and Van Dusen (1933) for 0°C were part of a series extending over the temperature range −78 to +31°C.   The weighted mean of 4 experimental results selected as the most reliable was 26 139·5 mmHg although the value calculated from an equation designed to fit the whole series was 26 141·7 mmHg.   Meyers and Van Dusen do not claim an accuracy better than about 1 part in 10^4 and it is pertinent to note that their *measured* value differs from the corresponding mean derived in the present paper by less than this amount.

Michels and his associates at the Van der Waals Laboratory, Amsterdam (Michels et al. 1950) included a group of three measurements using a triple point cell in the course of a series covering the range −56 to +3°C.   The mean of the three experimental results at 0·010°C was 34·4001 atm (26 144·1 mmHg) when double weight was given to one observation in which the pentane bath in the triple point cell was stirred, this value differing by less than 2 parts in 10^5 from our present result.   It may be noted that if the *same* weighting were given to all three results their value would become 34·4003 atm in which case the discrepancy is reduced to only about 1 part in 10^5.

It would be difficult now to establish with certainty the causes of the differences between the various results, but there are some fairly clear indications.   The precautions taken to secure adequate purity of the carbon dioxide were such that the presence of impurities can probably be discounted as an important cause of variation.   The most significant discrepancy, exceeding 25 parts in 10^5, is that between Bridgeman's results and those of the two latest studies.   The existence of systematic differences between results obtained with different pressure balances in Bridgeman's series points strongly to uncertainty in pressure standards as a major cause of this discrepancy.   There have been significant improvements in this regard during the last few decades.   Finally, in so far as temperature uncertainties may be involved, the two later results, in which a triple point cell was used for controlling the temperature, are probably the least subject to error in this respect.

4. Conclusions

The main purpose of the work described in this paper was to assist in resolving some significant discrepancies in the published values of the vapour pressure of carbon dioxide at or near 0°C, in the light of the suggestion by Bridgeman (1927) that this quantity be adopted as a reference pressure for calibration purposes.   The mean 29 of measurements at 0·01°C, 3·485 64 MN m^{-2} with estimated limits of accuracy ±0·000 12 MN m^{-2}, agrees to better than 2 parts in 10^5 with the value stated by Michels et al. (1950), and does not differ from the experimental result of Meyers and Van Dusen (1933) by more than the somewhat wider limits of uncertainty claimed by those authors.   The new value departs from that of

Bridgeman, however, by more than 25 parts in 10^5 and it is concluded that this difference must be attributed, in the main, to the improvements which have been introduced in standards of high pressure measurement since the time of the earlier work.

Acknowledgments

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