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Measurement of high pressures by electrolyte conductance

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A simple electrolyte conductance cell is described which can be used as a secondary reference pressure gauge. With a dilute acetic acid solution in the cell, and referring to a manganin coil gauge as the pressure standard, in the pressure range 1000–3000 atmospheres the standard deviation in pressure measurements ranged from 0·35% at 1000 atmospheres to 0·25% at 3000 atmospheres. The electrolyte cell is free from hysteresis and strain effects and is a small and easily transportable unit.

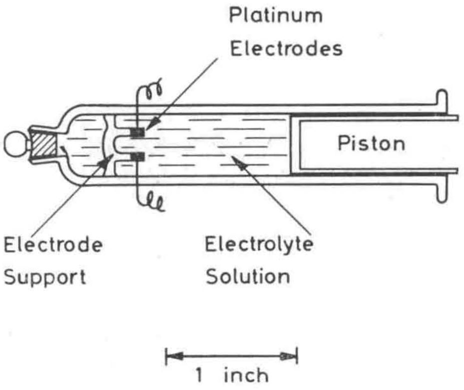
1. Introduction

Two types of secondary gauges are in general use for measuring pressures of the order of several thousand atmospheres (Bridgman 1952, Hamann 1957). The cheapest form, the Bourdon gauge, can seldom be relied upon to indicate pressures more accurately than to ±0·5%, and then only with frequent standardization. A manganin resistance gauge, with careful construction, is capable of indicating pressures in the above range within ±0·1%. The pressure coefficient of resistance for manganin varies slightly with the history of the wire. Pressure gauges based on the compression of fluids have also been suggested but have found little use. Gauges, operating by means of a strain gauge showing the deformation of a cylinder under pressure, are now available commercially with a precision only slightly less than a manganin resistance gauge. Primary standardization in each case is against a gauge involving the free piston, or summation of mercury column principles.

Recently several papers have been published on the change with pressure in the conductance of electrolyte solutions (Hamann 1957, Ellis 1959, Clark and Ellis 1960). The changes in conductance at 25° C for an increase of 1000 atmospheres range from a few per cent for 'strong' electrolytes such as KCl and HCl up to a factor of about two for the weak electrolyte system (CO_2–H_2O). It appeared that a secondary pressure gauge could be developed, using as a basis the change in conductance of an aqueous weak electrolyte solution with pressure. Results are now presented to show that with a dilute solution of acetic acid in a simple conductance cell pressures relative to those shown by a manganin coil gauge can be reproduced in the range 1000–3000 atmospheres with a standard deviation ranging from 0·35% at 1000 atmospheres to 0·25% at 3000 atmospheres.

2. Experimental

The conductance cell consisted of a 5 cm^3 Pyrex syringe with a tight-fitting ground glass piston and cylinder, adapted as shown in the figure. The cell constant was $1{\cdot}217\ cm^{-1}$. The platinum electrodes were fixed around a glass U-piece to anchor them firmly, and before use they were lightly coated with platinum black. Providing that the platinum lead-in wires through the glass are of small diameter (about 30 s.w.g.) there is no danger of the cell cracking at pressures of 3000 atmospheres. The pressure vessel was as described earlier (Ellis 1959) and pressures were generated by a hand hydraulic pump and pressure intensifier using medicinal paraffin as the pressure medium. As a free piston gauge was not available the reference pressure standard was a manganin resistance gauge manufactured and supplied by Harwood Engineering Co. (Mass., U.S.A.), who calibrated the instrument against a primary standard accurate to within ±0·1–0·2% in the pressure range of interest. The thermostat was an oil-bath controlled at 25 ± 0·05° C. Resistances were measured with a 1000 c/s capacity-compensated Sullivan Wheatstone bridge.



Conductance cell adapted from 5 ml. syringe.

In each run the cell was filled with 0·05 M acetic acid and allowed to come to thermal equilibrium within the pressure vessel in the oil bath (2–3 hours). The cell resistance at 1 atmosphere was obtained, and the pressure increased to about 1000 atmospheres. After allowing time (30–40 minutes) for thermal equilibrium to be re-established, the pressure was read approximately on a Bourdon gauge and more precisely on the manganin gauge, and the cell resistance measured again. The process was repeated at about 2000 and 3000 atmospheres, then readings were taken about 2000 and 1000 and at 1 atmosphere on the return half of the cycle. A cycle was completed once a day for several days, then a new run with a fresh solution started.

Corrections to the resistances for distilled water blanks were not made as the whole cell contents are the mechanism of the suggested gauge. The distilled water would account for a maximum of 1% of the total conductance under the present conditions, its specific conductance at 25° C and 1 atmosphere being $1{\cdot}2 \times 10^{-6}\ ohm^{-1}\ cm^{-1}$.

3. Results

The results from four runs are given in table 1. The values of the cell resistance ratios R^P/R^1 about 1000, 2000 and 3000 atmospheres are given in brackets following the pressure (P) in lb in^{-2} gauge obtained from the manganin gauge. A mean line drawn through the results from 1–3000 atmospheres passes through values of R^P/R^1 of 0·7433, 0·5888 and 0·4837 at 14 696, 29 392 and 44 088 lb in^{-2} gauge respectively. Maximum deviations of the experimental R^P/R^1 points from this mean line were 0·75%, 0·50% and 0·30%, and their standard deviations were 0·35%, 0·29% and 0·25% at about 1000, 2000 and 3000 atmospheres respectively. Differences between runs were no greater than differences between cycles of the same run.

Table 1. Values of the cell resistance ratios R^P/R^1 (in brackets) at pressures in lb in^{-2} gauge about 1000, 2000 and 3000 atmospheres. Electrolyte 0·05 m acetic acid.

	Cycle	About 1000 atm.		About 2000 atm.		About 3000 atm.
		Increasing P	Decreasing P	Increasing P	Decreasing P	
	1	14 630 (0·7444)	15 180 (0·7378)	29 070 (0·5927)	29 090 (0·5914)	42 930 (0·4912)
	2	14 810 (0·7419)	15 360 (0·7356)	29 480 (0·5878)	28 800 (0·5942)	42 500 (0·4942)
Run 1	3	14 780 (0·7414)	14 680 (0·7435)	29 410 (0·5881)	29 230 (0·5902)	42 530 (0·4939)
	4	14 850 (0·7407)	14 610 (0·7456)	29 380 (0·5884)	28 510 (0·5970)	43 020 (0·4918)
	5	14 720 (0·7435)	14 430 (0·7469)	28 690 (0·5957)	29 520 (0·5885)	43 510 (0·4888)
	1	14 570 (0·7460)	14 630 (0·7440)	29 230 (0·5912)	29 600 (0·5873)	43 990 (0·4848)
Run 2	2	14 940 (0·7411)	15 260 (0·7373)	29 550 (0·5885)	30 170 (0·5830)	43 610 (0·4878)
	3	14 690 (0·7427)	14 860 (0·7412)	29 110 (0·5920)	30 270 (0·5812)	42 750 (0·4939)
	4	14 550 (0·7452)	14 840 (0·7417)	29 370 (0·5897)	29 170 (0·5912)	43 670 (0·4874)
	1	14 530 (0·7452)	14 430 (0·7458)	29 130 (0·5897)	29 550 (0·5864)	44 440 (0·4803)
Run 3	2	14 470 (0·7455)	14 820 (0·7414)	29 000 (0·5918)	29 420 (0·5876)	44 540 (0·4803)
	3	14 690 (0·7432)	14 920 (0·7404)	29 480 (0·5873)	29 300 (0·5882)	42 300 (0·4958)
Run 4	1	14 730 (0·7432)	14 690 (0·7438)	29 470 (0·5880)	29 580 (0·5874)	43 790 (0·4852)
	2	14 920 (0·7404)	14 700 (0·7432)	29 470 (0·5877)	29 540 (0·5870)	43 930 (0·4838)
			Mean value of R^P/R^1 at 14 696 lb in^{-2} gauge 0·7433	Mean value of R^P/R^1 at 29 392 lb in^{-2} gauge 0·5888		Mean value of R^P/R^1 at 44 088 lb in^{-2} gauge 0·4837

As a further test the apparatus was cycled once a day between 1 and exactly 14 696 lb in^{-2} gauge, using the same solution of acetic acid. Table 2 shows the resistance ratio results obtained.

Table 2.

R^P/R^1	0·7445	0·7436	0·7435	0·7438	0·7431	0·7431	0·7435
No. of cycles	1	2	3	4	5	6	7

These values show a standard deviation from the average of 0·06%, and after the first cycle there is little trend with time. During the week the overall resistance of the cell at 1 atmosphere rose by 0·3% from 3355 to 3366 ohms. This trend with time was noticed on all runs of several days' duration. Filling the cell with fresh acetic acid solution always restored the cell resistance to 3350 ± 10 ohms.

4. Discussion

The present results show that the weak-electrolyte cell could be a useful addition to the range of secondary pressure gauges. Points in favour of a weak-electrolyte pressure indicator are the large changes in measured variable with pressure, the ease of preparing the cell and the fact that there are no difficulties with metal strain as with manganin. Although the sensitivity of the gauge, at least with acetic acid, is not much better than a Bourdon gauge, it has stability and a lack of hysteresis. As with the manganin gauge, pressure is directly related to a physical property of a material. Fatigue of mechanical systems such as with the Bourdon and strain-gauge-on-cylinder type of gauges is avoided.

Disadvantages are that the pressure indicating medium is not permanent (the solution should be replaced when the one atmosphere conductance value changes by more than about 1%), the relationship between resistance and pressure is not linear and a rather long time is necessary after pressure changes to allow thermal equilibrium to be re-established. It is doubtful whether the cell could be used above 4000–5000 atmospheres because of cracking at the platinum–glass seal. The temperature must be controlled to about ±0·05 degc if errors in pressure due to temperature fluctuations are to be kept below 0·1%. The actual temperature is not so critical (somewhere between 24·7–25·3° c).

In direct comparison with the manganin gauge the electrolyte cell now described is slightly lower in sensitivity, but possibly may be made equivalent with refinement of technique. The pressure range it can cover is lower, and it is rather fragile compared with the manganin cell. Its ease and cheapness of construction from laboratory materials should make it immediately valuable for small laboratories who wish to standardize high-pressure Bourdon gauges to a moderate degree of accuracy without the expense of buying a manganin gauge. The large pressure coefficient of resistance change and lack of strain effects suggest a potential in the electrolyte method which warrants extensive investigations of the type that went into the development of the manganin gauge.

Acetic acid was used as an electrolyte in this initial work as it is a substance easily purified, readily available and with a convenient degree of ionization ($K_a = 1{\cdot}75 \times 10^{-5}$ at 25° c). A trial with ammonia, which has a similar ionization constant, was not so satisfactory due to an appreciable zero drift (several per cent) over a week's cycling. This effect cannot be simply explained as the percentage drift was much greater at 1 atmosphere than at 3000 atmospheres, but it was probably related to alkaline attack on the glass cell. If this drift could be eliminated, a dilute ammonia solution would be a more sensitive pressure indicator as its change in conductance with pressure (Hamann 1957) is three times as great as that for acetic acid.