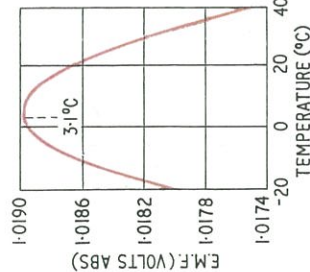
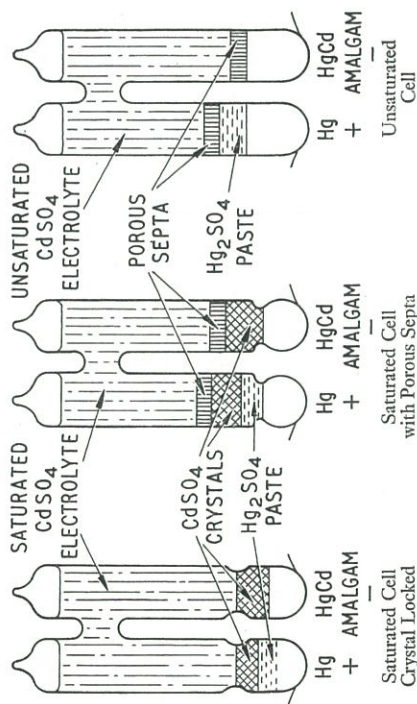
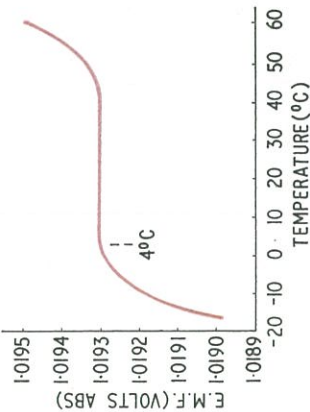
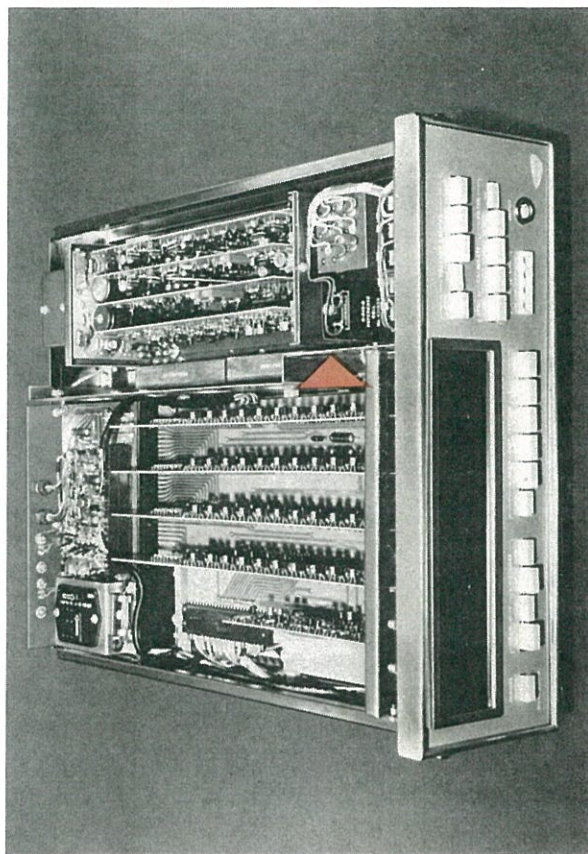


FIG. 1 TYPICAL CONSTRUCTIONS

FIG. 2
E.M.F.-Temperature Curve,
Saturated Cell, Acidity 0.05 N.FIG. 3
Typical E.M.F.-Temperature
Curve, Unsaturated Cell.

lated from the internationally adopted formula based on the work of Wolff. (1)
 $\Delta e = -40.6(t-20) - 0.95(t-20)^2 + 0.01(t-20)^3$
 where Δe is the divergence in microvolts from the e.m.f. at 20°C (see T.C. curves, Figs. 2 and 3).
 Acidity of electrolyte. Neutral cells have been completely superseded by cells containing a specific low concentration of sulphuric acid in the electrolyte to prevent hydrolysis of the depolarising agent (mercurous sulphate). It was found that acid cells display a greater stability, less temperature hysteresis and a greater constancy of e.m.f. among individual cells in a group. For many years it was normal practice to use an acidity of 0.1 N but experience in the field showed that many failures occurred due

to excessive "gassing" at the cadmium amalgam surface. About ten years ago an acidity of 0.05 N was adopted. This has proven entirely successful and no further failures due to trapped gas bubbles leading to variations in internal resistance and fluctuations of e.m.f. have been reported. It is worthy of note that the e.m.f. of a saturated standard cell is affected by change of acid concentration.
 Neutral Cells 1.01865 Volts Absolute at 20°C
 0.05 N Acid Cells 1.01862 Volts Absolute at 20°C
 0.1 N Acid Cells 1.01859 Volts Absolute at 20°C
 Amalgam Concentration. The e.m.f. of the cadmium amalgam electrode is virtually independent of the cadmium concentration provided that both solid and liquid phases are present together. This condition exists over a range of approximately 50°C but the lower and higher temperature limits may be shifted by varying the concentration. It is normal practice to utilise a 10% cadmium amalgam for saturated cells which have a working range of approximately 0°C - 40°C whereas a concentration of 12% is generally used in unsaturated cells as in industrial applications higher operational temperatures are often encountered.



Fenlow Electronics Ltd.—Digital Voltmeter. Arrow indicates position of the Muithead D-845-D Reference Cell.

plate electrolyte it is evident that at the same temperature saturated and unsaturated cells have a different e.m.f.
 General Construction. Saturated and unsaturated cells are normally made in hermetically sealed 'H' shaped glass containers with a platinum lead-in wire sealed through the base of each limb. The mercury cathode is at the lower end of one limb covered with a layer of mercurous sulphate in direct contact. The cadmium amalgam anode is at the lower end of the other limb. The electrolyte which is an acidified solution of cadmium sulphate fills the container to above the cross arm. In the case of the saturated cell an excess of solid crystals of cadmium sulphate are present to ensure saturation at all working temperatures. Porous septa of an inert material are normally incorporated to retain the solid constituents in position during transport. (Fig. 1 shows typical constructions.)
 Temperature Coefficient (T.C.). The T.C. of e.m.f. of unsaturated cells is considerably lower than that of saturated cells. In cells of both types the T.C. of each individual limb is high but of opposite sign

and the sum of the two coefficients gives the overall T.C. In the case of the saturated cell at 20°C the T.C. of the mercury limb is approximately +310 $\mu V/^\circ C$ whereas that of the cadmium limb is approximately -350 $\mu V/^\circ C$ thus giving an overall T.C. of -40 $\mu V/^\circ C$. It may be noted that the T.C.s vary slightly with temperature and at 30°C the T.C. of the mercury limb is approximately +330 $\mu V/^\circ C$ and that of the cadmium limb approximately -380 $\mu V/^\circ C$ thus giving an overall T.C. of -50 $\mu V/^\circ C$. In a cell in which the electrolyte is unsaturated at all working temperatures the cadmium sulphate concentration remains constant. This results in a substantially lower overall T.C. It is, in fact, possible to arrive at a specific concentration so that the changing T.C. of the mercury limb is exactly compensated and the overall T.C. is exactly zero over a wide operational temperature range. When this condition is attained the individual T.C.s of both limbs are approximately +395 $\mu V/^\circ C$ and -395 $\mu V/^\circ C$ respectively at 20°C. At 4°C and below the unsaturated cell becomes saturated and behaves accordingly. The e.m.f. of the saturated cell at any temperature between 0°C and 40°C can be calculated

which applies to both types of cell is the change of concentration of mercurous sulphate in the electrolyte in the vicinity of the cathode with a change of temperature. The effect is much worse with a fall in temperature as supersaturation requires a longer time to reach equilibrium. Hysteresis in cells is influenced considerably by physical size and internal construction. The introduction of mechanical septa to retain the solid constituents of cells in position during transport invariably increases hysteresis but this may be kept to a minimum with the right choice of material and design. For many years it has been accepted practice in the construction of the highest precision standard cells to avoid the use of mechanical septa. This is accomplished by sin- tering the cadmium sulphate crystals into a hard porous plug by a heat and evaporation technique known as crystal locking. Unfortunately the resultant internal resistance is not easily predictable and invariably increases slowly with age, the hysteresis characteristic also following a similar pattern of behaviour. This is mainly due to the long electrolyte paths through the sintered crystal packs becoming progressively smaller with continuing crystal