

obtained for one of them. It is seen that  $R$ , and hence the value of  $n_f$ , remains substantially constant up to about 150° C., but that above this temperature the value of  $|R|$  decreases rapidly, indicating a sharp increase in  $n_f$ . The variation of  $|R|$  with oxygen pressure,  $P_{O_2}$ , at constant temperature (plotting air pressure as its partial pressure of oxygen) is found to agree with the equation

$$\log |R| = \frac{1}{n} \log P_{O_2} + \text{const.}$$

previously suggested by me<sup>4</sup>, using Wagner's relation that

$$n_f = KP_{O_2}^{-1/n},$$

where  $K$  is an equilibrium constant for the reaction between oxygen and cadmium oxide, and  $n$  is a constant, the value of which can be predicted from arguments based on chemical thermodynamics. Previous results of Wagner and his co-workers<sup>5,6</sup> show that the experimentally determined values of the constant  $n$  decrease with increasing temperature. The values calculated from Fig. 2 are as follows:

Temperature (°C.)	148	185	202
Value of $n$	14.6	10.6	6.6

These values are of the same order as those obtained by Baumbach and Wagner from measurements of the variation of the conductivity of cadmium oxide with oxygen pressure<sup>5</sup>.

The value of free-electron concentration at a pressure of 774 mm. of air and from room temperature up to 150° C. is approximately  $3.4 \times 10^{18}$  per cm.<sup>3</sup>. Although this value is high for a semi-conductor, it is not considered sufficiently high to explain completely the degeneracy observed at such low temperatures and the subsequent increase in  $n_f$  at about 150° C. The influence of the above results on the interpretation of the conduction processes in cadmium oxide will be published elsewhere.

These experiments were carried out in part at Queen Mary College, London, and completed while at Chelsea Polytechnic. Thanks are due to Prof. H. R. Robinson and to Dr. W. H. George for the provision of laboratory facilities.

C. A. HOGARTH

Physics Department,  
University, Reading.  
Nov. 18.

<sup>1</sup> Meyer, W., *Z. Elektrochem.*, **50**, 274 (1944).

<sup>2</sup> Andrews, J. P., *Proc. Phys. Soc.*, **59**, 990 (1947).

<sup>3</sup> Wright, E. W. H., thesis, London (1949).

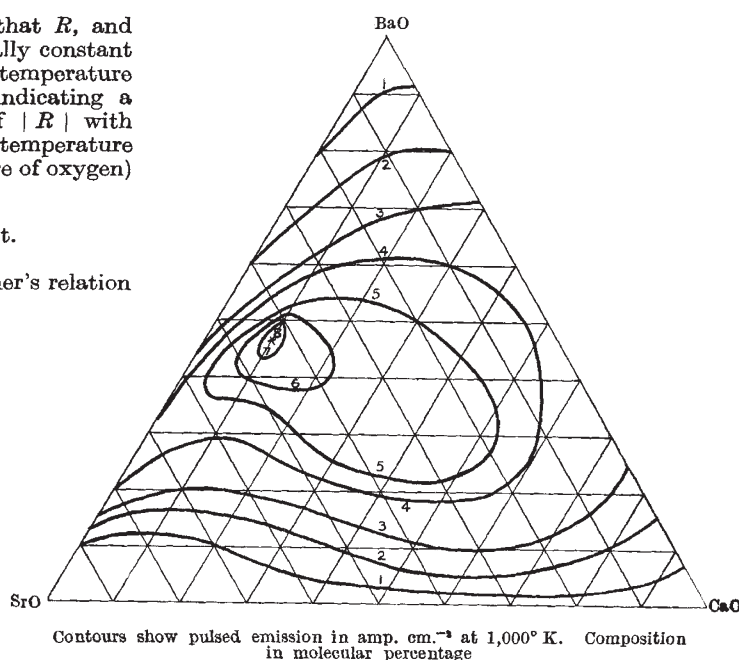
<sup>4</sup> Hogarth, C. A., *Phil. Mag.*, **39**, 260 (1948).

<sup>5</sup> von Baumbach, H. H., and Wagner, C., *Z. phys. Chem.*, **B**, **22**, 199 (1933).

<sup>6</sup> von Baumbach, H. H., and Wagner, C., *Z. phys. Chem.*, **B**, **24**, 59 (1934).

### Pulsed Emission from the BaO-SrO-CaO System

IN a recent communication<sup>1</sup> we referred to our work on the measurement of the thermionic emission from mixtures of alkaline earth oxides (BaO, SrO and CaO). The accompanying diagram shows the variation of pulsed emission (amp. cm.<sup>-2</sup> at 1,000° K.) with molecular composition which we have found. As can be seen, there appears to be a large central area in which the emission is greater than the maxi-



Contours show pulsed emission in amp. cm.<sup>-2</sup> at 1,000° K. Composition in molecular percentage

mum obtained from any barium/strontium mixture. A maximum of about 8.0 amp. cm.<sup>-2</sup> occurs at BaO : SrO : CaO : : 47 : 43 : 10, the emission falling away sharply with any variation of composition greater than 2 per cent. This value has been obtained from oxides prepared from either mixed or co-precipitated carbonates and can be repeated to within  $\pm 10$  per cent. Violet and Reithmuller<sup>2</sup> have also found a similar variation of emission in the neighbourhood of this composition. In all, about a hundred different compositions have been studied, in many cases from both mixed and co-precipitated carbonates.

No theoretical explanation can at present be offered; but X-ray examinations, a study of the life performance, and other experiments are in hand.

L. ELIZABETH GREY

Research Staff of the M.O. Valve Company  
at the Research Laboratories,  
The General Electric Co., Ltd.,  
Wembley.

<sup>1</sup> Grey, L. E., *Nature*, **165**, 773 (1950).

<sup>2</sup> Violet, F., and Reithmuller, J., *Ann. Radioelect.*, **4**, 184 (1949).

### Origin of a Time-lag Effect in Selenium Rectifiers

It is a rather common occurrence that the resistance of semiconductor rectifiers drifts after application of a voltage. This effect is particularly strong immediately following the application of a voltage in the blocking direction. If the current decreases with time, one speaks of 'forming'; if it increases, of 'creep'. Forming and creep effects are particularly large in selenium rectifiers<sup>1</sup>. An explanation has been proposed<sup>2</sup> based on the migration of ions in the barrier layer of the rectifier.

A time-lag between a voltage change and the resulting change of impedance of selenium rectifiers is indicated by the different values of impedance obtained from the following two measuring methods: (a) the rectifier is part of an audio-frequency bridge using a small