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EFFECT OF OXYGEN ON ELECTRON CAPTURE DETECTION

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SUMMARY

It appears that if the carrier gas does not contain electronegative contaminants the electron concentration in the electron capture detector is virtually independen of the temperature and the gas flow-rate. With oxygen in the carrier gas, the electro concentration decreases. During elution of other electronegative components, oxyge causes charge transfer to occur. Depending on the temperature, this effect seem to increase the sensitivity of the detector to such components.

INTRODUCTION

WENTWORTH and co-workers[1–3] described a set of reactions that take plac in the electron capture detector and which give a satisfactory explanation of severa properties of the detector. DEVAUX AND GUIOCHON[4–9] carried out experimenta studies on the practical application of the detector. Some of the phenomen observed, notably the dependence of the electron concentration inside the cell o the gas flow-rate, cannot be directly explained from the reaction equations propose by WENTWORTH.

In much of the previous experimental work, insufficient attention has bee given to the presence of oxygen as an electronegative contaminant in the carrie gas.

Thermal electrons react with oxygen according to the equation[10–12]

$$M + O_2 + e^- \rightarrow M + O_2^- \quad (1$$

The reverse reaction can also take place:

$$M + O_2^- \rightarrow M + O_2 + e^- \quad (2$$

Direct dissociation takes place only in the presence of electrons that hav an energy greater than 3.5 eV (ref. 13).

It is known that the simultaneous presence of a halide in the gas gives ris to charge transfer according to the equation[13]

$$O_2^- + RX \rightarrow R^{\cdot} + X^- + O_2 \quad (3$$

Depending on the type of halide, this reaction may be accompanied by dissociative electron attachment:

$$RX^{l} + e^{-} \rightarrow R^{\cdot} + {}^{l}X^{-} \qquad (4)$$

As a result of reactions 1 and 2, the electron concentration will decrease. The degree to which the electron-generating reaction 2 will proceed depends on the electron-preserving reaction 3. The electron capture efficiency of oxygen is defined by the type and capture of the halide.

EXPERIMENTAL

Both argon–methane and nitrogen were used as the carrier gas. Oxygen was removed by passing the carrier gas over copper at 475°. Water and other impurities, if any, were subsequently eliminated by means of an activated molecular sieve. The clean carrier gas was fed into a MicroTek ^{63}Ni pin-cup electron capture detector (10 mCi source).

The detector outlet was connected by means of metal tubing with either an oxygen meter (Hersch cell) or a water meter[14]. The space around the detector was purged with oxygen-free nitrogen. Liquid electronegative components were added to the carrier gas through a diffusion capillary[4]. The oxygen content of the exit gas was less than 0.5 p.p.m., water content *ca.* 3 p.p.m.

Oxygen was supplied through a PTFE tube section placed in the feed line before the molecular sieve column. The PTFE tube was surrounded by a blanket of oxygen, which diffused into the carrier gas through the wall. The desired oxygen concentration was obtained by varying the length of the PTFE tube. The detector was operated entirely on the pulse principle. The pulse generator of the electron capture detector being inadequate for this purpose, it was replaced by a Philips GM 2314 unit, which has a wider range and which operated satisfactorily.

The signal was measured on a Keithly 417 K chromatograph electrometer and registered by a Servogor recorder, Type RE 511.

RESULTS AND DISCUSSION

Measurements in pure carrier gases

With the pulsed mode of operation, the pulse width is chosen such that all electrons in the reaction zone will have sufficient opportunity to collect on the anode. This width is dependent on the potential difference between the electrodes and on geometric factors.

Fig. 1 shows the relation between the pulse width and the number of electrons captured in one pulse. The results of WENTWORTH *et al.*[1], in conjunction with our curves in Fig. 1, indicate that the field intensity in the cell is low and, at the same time, is distributed non-homogeneously.

The variation of the electron concentration after the pulse is given by the following equation:

From the experimental relation, shown in Fig. 2, the thermal electron production and the rate constant of the termination reaction were calculated (Table I).

The magnitude of k_D varies with the concentrations of the positive ions and radicals. There will certainly exist some relation between these concentrations and the cell geometry; hence k_D also depends on the type of cell. A further cause of the differences between the experimental k_D values is the unwanted presence of electronegative components in the carrier gas, which manifests itself in too high values of k_D, implying that the standing current is too low. In particular, the discrepancy between our results and those published by DEVAUX AND GUIOCHON[9] have to be explained in this way, as they were all obtained on the same type of detector. The difference in methane concentration cannot be considered to be the cause[1].

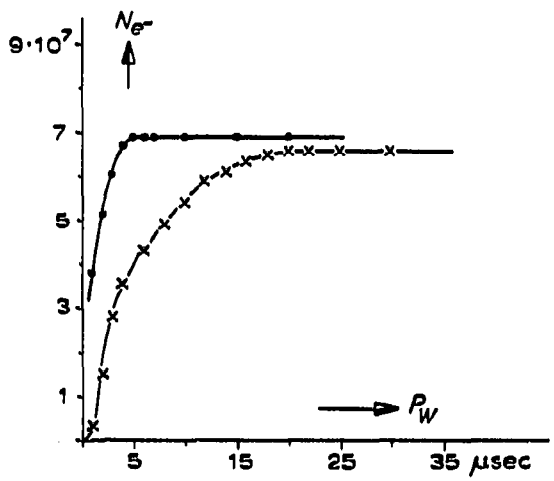


Fig. 1. Number of electrons collected *vs.* pulse width. ●, Argon + 10% methane; ×, nitrogen. Pulse period, 5000 μsec; applied potential, 40 V; temperature, 25°; flow-rate, 6 l/h.

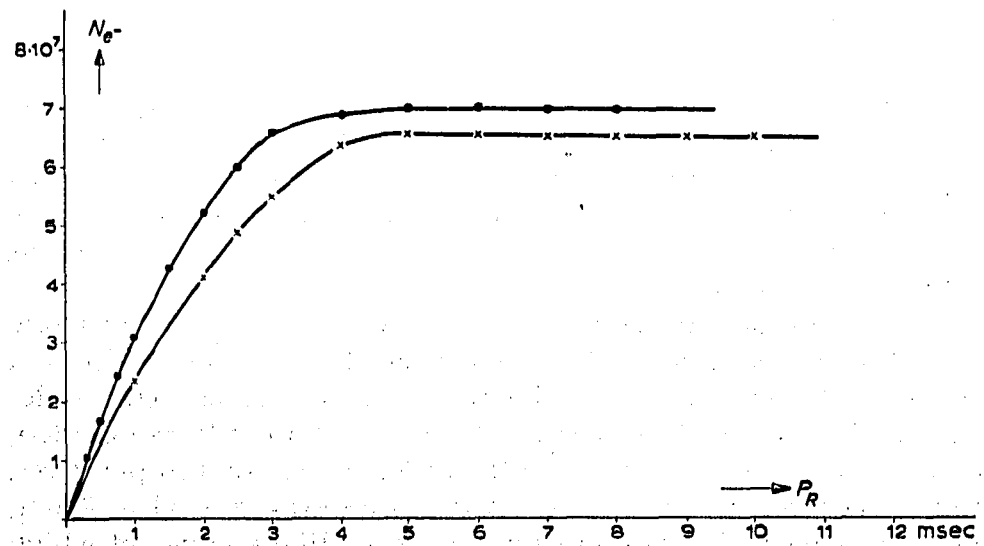


Fig. 2. Number of electrons in the cell *vs.* time after pulsing (clean carrier gases). ●, Argon +

TABLE I

RESULTS FOR RATE CONSTANT OF TERMINATION REACTION AND RATE OF PRODUCTION OF THERMAL ELECTRONS

	$k_D \cdot 10^{-3}$ (sec^{-1})	$k_p R_\beta \cdot 10^{-10}$ ($electrons \cdot sec^{-1}$))
Present study: Ar + 10% CH_4	0.5	3.5
WENTWORTH *et al.*[1]: Ar + 10% CH_4	2.4	—
WENTWORTH *et al.*[1]: Ar + 5% CH_4	1.7	—
DEVAUX AND GUIOCHON[9] Ar + 5% CH_4	10–20	2.5

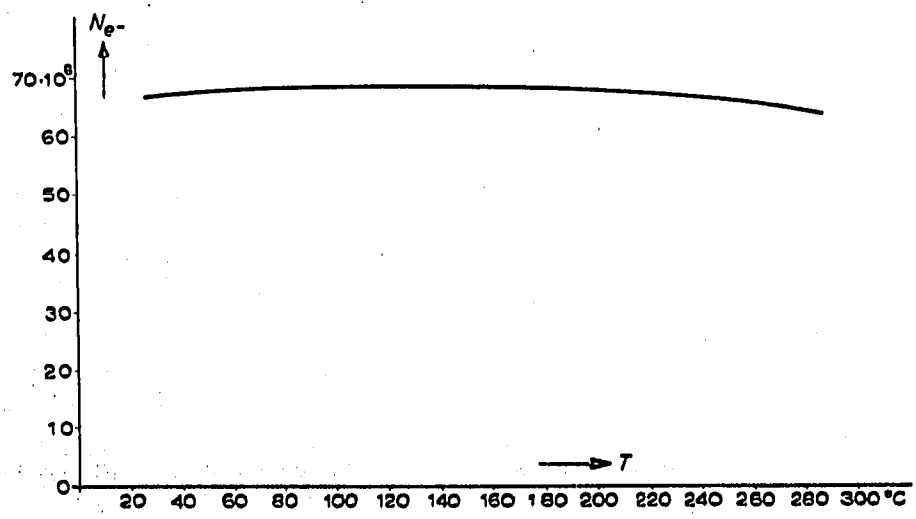


Fig. 3. Number of electrons in the cell *vs.* temperature. Carrier gas, nitrogen; flow-rate, 6 l/h; pulse rate, 6000 μsec; pulse width, 20 μsec.

Fig. 3 shows the relation between standing current and temperature. The pulse rate was such that equilibrium was established between each two pulses. The standing current appeared to be only slightly temperature-dependent, as was also noted by PETTITT[15] and SIMMONDS *et al.*[16]. However, the small dependence found by these workers can partly be ascribed to the unduly low pulse rate at which they conducted their experiments.

It is known that both the disintegration rate and the energy of the primary electron is independent of the temperature[15]. The energy needed for the production of an ion pair is defined solely by the nature of the gas. $k_p R_\beta$ is temperature-independent, as is k_D (ref. 1). On the basis of WENTWORTH's model, it must be concluded, therefore, that the electron concentration is virtually independent of temperature. This is confirmed by Fig. 3. The results of DEVAUX AND GUIOCHON[9] reveal a strong increase in the standing current with the temperature, the most likely cause of which is the presence of contaminants that have a non-dissociative electron capture

Electron capturing properties of oxygen

Oxygen has a large influence on the standing current. Contamination of the nitrogen carrier gas by 10 p.p.m. reduces the standing current by more than half (Fig. 4). Replacement of the nitrogen with argon–methane produces practically the same effect. Hence, to obtain a high standing current, drastic removal of oxygen is essential. Fig. 4 exhibits an irregularity at higher oxygen concentrations, which WENTWORTH *et al.*[1] ascribed to the effect that the periodic polarization of the

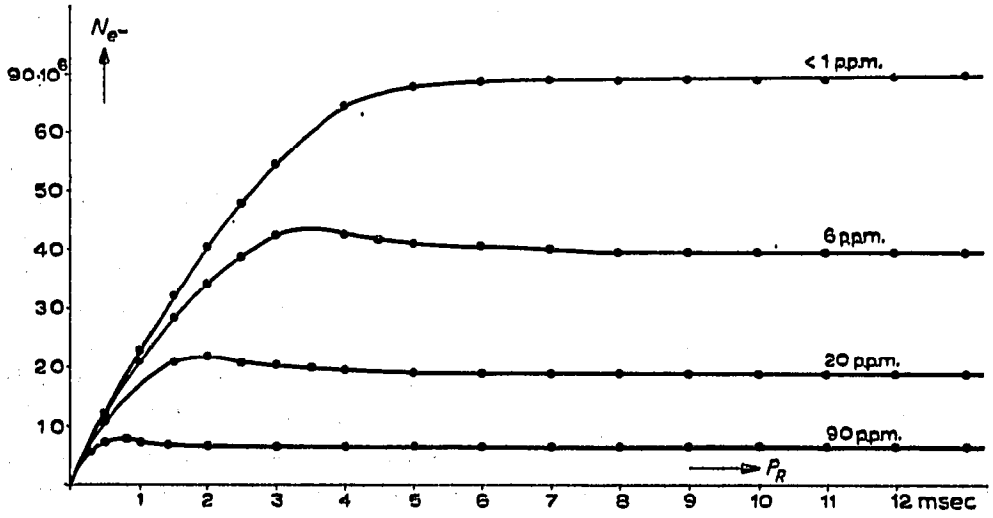
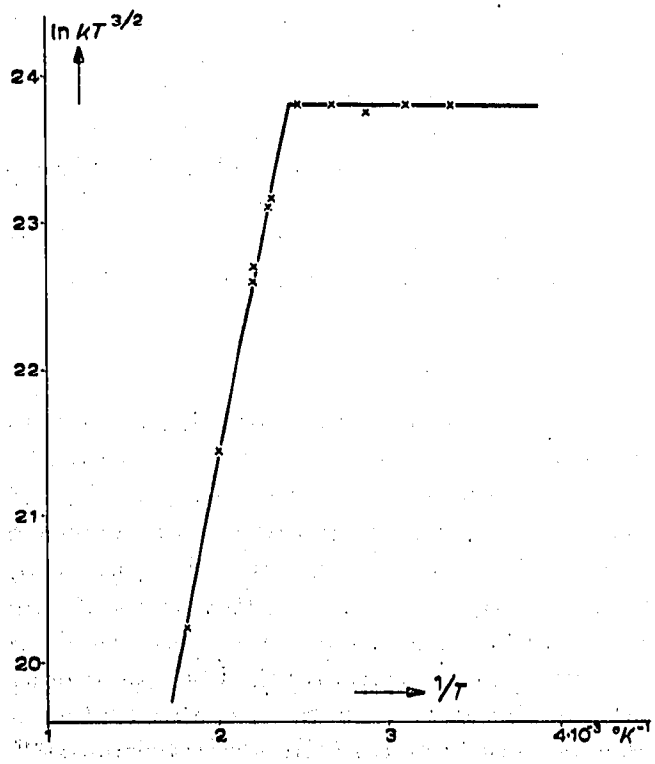


Fig. 4. Number of electrons *vs.* pulse rate for different oxygen concentrations. Carrier gas, nitrogen; flow-rate, 6 l/h; temperature, 80°; applied potential, 40 V; pulse width, 20 μsec.



electrodes has on the ionic concentration. The temperature-dependence of the electron capture coefficient is characteristic of the attachment mechanism[3]. The relation between oxygen concentration and temperature is shown in Fig. 5.

The electron capture coefficient hardly varies with temperature up to 150°; above this temperature the coefficient decreases as the temperature increases. The experimental results are in good agreement with known information about the electron attachment of oxygen. The course of the curve in Fig. 5 furnishes evidence of the formation of O_2^- (ref. 3). At 150° the detachment reaction 2 begins to play a part, which manifests itself in a decrease in k. With an O_2–CO_2 mixture, PACK AND PHELPS[17] noticed appreciable electron detachment above 160°. The electron affinity calculated from the positive slope in Fig. 5 (ref. 1) is 0.5 eV; PACK AND PHELPS[17] give a value of 0.43 eV.

It should be noted that the shape of the curve in Fig. 5 is also defined to some extent by the presence of water in the carrier gas. Even at very low water concentrations, ions are subject to hydration[10,12]. This will have an effect on the rate of reaction 2. The water concentration in our investigation was 3 p.p.m. Electron attachment of water is negligible[10], although reference has been made to the electron capturing properties of water[4,8]. O_2^- ions react readily with, *e.g.*, halogenated hydrocarbons. In practice, this is seen at higher temperatures in those instances in which the influence of oxygen on the standing current is small. During the detection of a halogenated hydrocarbon in a carrier gas contaminated by oxygen, reaction 3 takes place, with the result that the efficiency of the electron attachment rises. The sensitivity to the components seems to have increased.

This effect was checked experimentally with butyl bromide. The magnitude of the electron attachment is such that the course of reaction 4 is not influenced by the consumption of RX in reaction 3. Butyl bromide was added to the carrier gas through a diffusion capillary, which reduced the standing current by *ca.* 50%. Upon addition of oxygen, the electron capture coefficient was calculated from the decrease in the standing current. Whereas in the absence of butyl bromide the values of $\ln kT^{3/2}$ at 210° and 290° were 21.8 and 20.1, respectively, the values found in the presence of butyl bromide varied between 23.6 and 24.4. At lower temperatures, oxygen mainly influences the standing current, but its chief effect at higher temperatures is to change the sensitivity to the component that is to be detected.

Flow dependence of the electron capturing process

The standing current and flow-rate in a pure carrier gas are not related. Experiments conducted at flow-rates of 6 and 0 l/h gave a difference of less than 1%. SCOLNICK[1] who studied the electron capturing process at reduced pressure found similar results. DEVAUX AND GUIOCHON[8] noted a decrease in standing current with a decrease in the flow-rate. We also found such a dependence when the detector was not placed in an atmosphere of the pure carrier gas. It appeared to be impossible to seal the detector so as to prevent ingress of oxygen. Similar difficulties were observed in another investigation conducted with a different type of detector[19]. The statement that the rate of recombination is influenced by the flow-rate to the effect that a high rate would result in a loss of positive ions is not confirmed by these experiments[20]

independent of the flow-rate. To prevent the concentration of the component from decreasing during the electron capturing process, use was made of a component that had a weak electron capturing capacity, *viz.*, acetic anhydride[21], which was added to the carrier gas through a diffusion capillary. The results are shown in Table II.

For components with a low degree of conversion, the detector acts as a concentration detector.

TABLE II

RELATION BETWEEN ELECTRON CAPTURE COEFFICIENT, k, AND FLOW-RATE, F

Detector temperature, 75°; carrier gas, Ar + 10% CH_4; pulse rate, 5000 μsec; pulse width, 5 μsec; applied potential, 40 V.

F (l/h)	c ($moles/l$)	k ($l/mole$)
2.1	$4.5 \cdot 10^{-7}$	$7.6 \cdot 10^{6}$
4.1	$2.3 \cdot 10^{-7}$	$7.8 \cdot 10^{6}$
5.9	$1.60 \cdot 10^{-7}$	$7.7 \cdot 10^{6}$

LIST OF SYMBOLS

c	Concentration
F	Flow-rate
k	Electron capture coefficient
k_D	Over-all rate constant of reactions with electrons
$k_p R_\beta$	Production rate of thermal electrons
N_{e^-}	Number of electrons in the cell
p_R	Pulse rate
P_W	Pulse width
t	Time

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