CHROM. 7451

HYPOTHETICAL MECHANISM OF THE HELIUM DETECTOR

OPERATION IN THE POSITIVE AND LINEAR MODES

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(Received January 31st, 1974)

SUMMARY

On the basis of the Townsend equation for the gas amplified current and of the Dutton–Powell equation for the enhancement of the primary ionization coefficient in gas mixtures due to the Penning effect, a mathematical model of the chromatographic helium detector is proposed. Because both calculations of the relative current increase for $E/p = 4$, 5 and 6 V/cm·torr and actual measurements lead to linear calibration graphs for the sample calibrations at the parts per million level, a simplified and linearized relationship was developed, although further experimental confirmation is needed. The suggestion is made that the derived equation will make possible measurements of the θ number of metastable states produced per electron per centimetre of drift in an electric field, and the cross-sections for the Penning effect. The rate constants for Penning ionization by triplet metastable atoms of helium for hydrogen sulphide and ethylene were evaluated but the results are of a relative character. The shortcomings of the model are considered: the lack of explanation of negative peaks, the role of specially added admixtures to the carrier gas, and no account of recombination phenomena are the most important. A brief scheme of necessary investigations is outlined.

INTRODUCTION

In gas chromatography, which is an instrumental method for the quantitative and qualitative analysis of gases and vapours, the helium detector is often used. Although it was introduced about 1960[1-6] and is now commercially available from Carlo-Erba (Milan, Italy)[7] and Varian Aerograph (Palo Alto, Calif., U.S.A.)[8-9], the mechanism of its operation is still not clear. Analyses with the helium detector are cumbersome because of the appearance of an anomalous negative signal. Attempts to explain the phenomena that occur in this detector have been undertaken[10-12], but they were mainly of a descriptive nature and were unsatisfactory. In general, the predominating opinion is that purity of the carrier gas is required for correct detector operation[4,8,10,13,14], but sometimes small amounts of gases such as hydrogen[7] or methane[15] (at the parts per million level) are added to helium in order to reverse the

polarity of the detector signal so that it becomes positive. If the detector works proper-ly and shows an increase in current in the presence of other gases in the helium flowing through it, then this is commonly attributed to the Penning effect[16].

In this paper we have attempted to verify the above idea and to find a quantitative dependence between the increase in current and the concentration of the added gas in the carrier gas of the helium detector, using the equation derived by Dutton and Powell[17] for the Towsend first ionization coefficient in a Penning mixture. The helium detector itself presents no problems as it has simple geometry —the two electrodes, each with a diameter of about 1 cm, are parallel, 1 mm apart, and polarization voltage is 400–500 V. One of the electrodes is covered with a beta-emitter (tritium of 250 mCi activity). The pressure inside the detector can be assumed to be atmospheric.

MATHEMATICAL MODEL

The Townsend equation has the form:

$$\frac{I}{I_0} = \frac{\exp(\alpha \cdot d)}{1 - \gamma\,[\exp(\alpha \cdot d) - 1]} \tag{1}$$

where

I = the gas amplified current flowing between the electrodes;
I_0 = the saturation current;
d = the electrode distance;
α = the Townsend first ionization coefficient;
γ = the generalized Townsend secondary ionization coefficient.

For a Penning mixture with a small level of admixture and for pressures close to atmospheric, Dutton and Powell[17] introduced the relationship

$$\alpha = \alpha_e + \theta P \tag{2a}$$

or

$$\alpha = \alpha_e (1 + KP) \tag{2b}$$

where

α_e = the first Townsend coefficient for pure helium, i.e., the number of ion pairs formed in collisions per electron per centimetre of its movement in the direction of the electric field;
θ = the number of metastable atoms produced per electron per centimetre drift in the direction of the field;
K = a constant for a given E/p and α_e, defined by the equation

$$\theta = K\alpha_e \tag{3}$$

P = the probability that a metastable atom will be destroyed in such a manner that an electron will be produced.

Dutton and Powell[17] assumed that this is possible only through the Penning effect between the impurity molecule and the metastable atom. They considered two metastable states, the 2^1S_0 singlet and the 2^3S_1 triplet, and hence P is the sum

$$P = f_s P_s + f_t P_t \tag{4a}$$

where

f_s, f_t = the fractions of θ metastable states produced per electron per centimetre that are singlets or triplets, respectively. It is therefore obvious that

$$f_s + f_t = 1 \qquad (4b)$$

P_s, P_t = the probabilities of the destruction of the singlet or triplet states, respectively, in the Penning effect.

Dutton and Powell[17] took into account the following three processes leading to the depopulation of the metastable states:

(1) a two-body process involving a neutral helium atom and a metastable atom;
(2) a three-body process involving two neutral helium atoms and a metastable atom;
(3) a two-body process involving an impurity molecule and a metastable atom, i.e., the Penning effect.

As a result, P_s and P_t have the forms

$$P_s = \frac{rQ_s v}{A_1 + B_1 N + rQ_s v} \qquad (5)$$

$$P_t = \frac{rQ_t v}{A_2 + B_2 N + rQ_t v} \qquad (6)$$

where

r	= the fractional concentration of impurity molecules;
v	= the average relative velocity of the colliding particles in the Penning effect;
Q_s, Q_t	= the cross-section for the Penning effect between the impurity molecule (only one admixture gas is assumed) and corresponding singlet or triplet states of helium;
A_1, B_1, A_2, B_2	= the rate coefficients for processes (1) and (2) listed above;
N	= the number of helium atoms per unit volume (1 cm^3).

NUMERICAL DATA FOR CALCULATIONS

A_1, B_1, A_2 and B_2 were given by Phelps[18] as $6 \cdot 10^{-15}$ cm^3/sec, 10^{-32} cm^6/sec, $2 \cdot 10^{-17}$ cm^3/sec and $2.5 \cdot 10^{-34}$ cm^6/sec, respectively. The value of $f_s = 0.3$ was also taken from the paper by Phelps[18] for the following range of E/N values: $8.4 \cdot 10^{-17} < E/N < 2.2 \cdot 10^{-16}$ V/cm^2. The values of α_e were calculated by Hughes[19] and are in good agreement with the previous work of Dunlop[20]. Hughes[19] also gave theoretical values of θ, which permit the calculation of $K = \theta/\alpha_e$ (ref. 21) to be made.

It was decided to carry out the calculation as if only one admixture gas (nitrogen) was added to helium, and to accept likewise, after Dutton and Powell[17], that $Q_t = 5.21 \cdot 10^{-16}$ cm^2 and $Q_s = 12.5 \cdot 10^{-16}$ cm^2 according to the results of Schmeltekopf and Fehsenfeld[22].

As the relative velocity between helium atoms and nitrogen molecules in thermal equilibrium at 293°K, the value $v = 1.32 \cdot 10^5$ cm/sec was accepted. The value $N = 2.7 \cdot 10^{19}$ cm^{-3} was used.

After inserting numerical data into eqns. 4a, 5 and 6, we obtained the equation:

$$P = 0.3\left(\frac{r}{r + 1.55 \cdot 10^{-3}}\right) + 0.7\left(\frac{r}{r + 9.1 \cdot 10^{-5}}\right) \tag{7}$$

The electric field in the helium detector is chosen in the range 3500–5000 V/cm, depending on the sensitivity required. Higher field values are not used because of instability of the detector base line. For this reason, the calculations were made for $E/p = 4$, 5 and 6 V/cm·torr. For these three values, the data on α_e/p, θ and K were taken from the paper of Hughes[19]. The K and α_e values accepted for calculation obtained for $p = 760$ torr are given in Table I.

TABLE I

VALUES OF K, α_e/p AND α_e FOR 760 torr USED IN CALCULATIONS

Parameter	E/p		
	4	5	6
α_e/p (cm^{-1}·torr^{-1})	10^{-3}	0.0037	0.007
α_e (cm^{-1})	0.76	2.81	5.32
K	118	53	31

In order to obtain the relationship between the increase in the ionization current of the detector and the nitrogen concentration in helium, it is necessary also to know the second Townsend coefficient, γ. Dutton and Rees[23] gave the variation of γ with E/p for helium for pressures slightly lower than atmospheric and obtained the values $\gamma = 4 \cdot 10^{-2}$ for $E/p = 4$ and 5 V/cm·torr. They observed the independence of this coefficient from the pressure in the range from 350–550 torr for $E/p = 4$ V/cm·torr. The same order of magnitude was obtained by Dutton et al.[24] for helium containing 5% of neon, but they obtained a dependence of γ on the type of cathode and the manner of processing the cathode. Dutton et al.[25] observed an increase in γ with an increase in helium purity of nearly two orders of magnitude from 10^{-3} to 10^{-1} for $E/p = 3.5$ V/cm·torr and a pressure of 150–560 torr. Considering gases other than helium, it is worth mentioning the papers by Heylen[26,27] in which a strong and complicated dependence of γ on the pressure and hydrocarbon admixtures in argon is given, and also experiments with nitrogen by Folkard and Haydon[28] and Haydon and Williams[29] showing the dependence of γ on the electrode distance and gas impurities.

To summarize, the second generalized Townsend ionization coefficient can vary with many factors, such as pressure, the type and amount of admixtures, electrode distance and the material and state of processing of the electrodes. It is not known under which conditions each of these factors is the most important or the nature of the interactions that determine γ, especially the role of metastable atoms, although there are papers[28-31] in which their importance in this process is shown. Owing to this situation, it was decided to carry out the calculations for $\gamma = 1, 0.3, 0.01, 0.003$ and 0.001.

RESULTS AND DISCUSSION

As the helium detector signal is the increment of the current above the background, caused by the introduction of a sample containing a certain concentration of the investigated compound into the carrier gas, the following equation was used in the calculation:

$$\frac{\Delta I}{I_0} = \frac{I - I_b}{I_0} \tag{8}$$

where

I = the detector current in the presence of nitrogen with a fractional concentration r in the carrier gas;

I_b = background current for ideally pure helium, i.e., $r = 0$ and $\alpha = \alpha_e$. $\gamma = \gamma_e$.

Then

$$I_b = \frac{\exp(\alpha_e \cdot d)}{1 - \gamma_e [\exp(\alpha_e \cdot d) - 1]} \tag{9}$$

The results of the calculation are presented in Fig. 1a, 1b and 1c in the sequence $E/p = 4$, 5 and 6 V/cm·torr. They were obtained on an ODRA-1304 computer for r changing by one tenth of the given range from 10^{-9} to 10^{-3}. Points at which the curves end are the last within the accepted step, before theoretical breakdown (for eqn. 1 and the numerical data given above). These plots show that the growth of the current is linear for all values of E/p and γ in the nitrogen concentration range from 1 to 100 ppb*, and departure from linearity and faster enhancement of the current with the impurity concentration are the greater the larger are E/p and γ. The smaller are γ and E/p, the longer is the curve in the direction of higher concentrations.

At the same time, a change in γ from 0.01 to 0.001 is unimportant, especially for small concentrations.

Linearization of the equation for the helium detector signal at small concentrations

Because of the initial linear part of the curves shown in Fig. 1, an attempt can be made to convert eqn. 8 for the relative current increase with the impurity concentration into a linear function. Using the expansion of the exponential function and taking only the two first terms:

$$\frac{I}{I_0} = \frac{1 + \alpha d}{1 - \gamma \alpha d} = (1 + \alpha d) \cdot (1 + \gamma \alpha d) \tag{10}$$

and, neglecting terms containing $(\alpha d)^2$:

$$\frac{I}{I_0} = 1 + (1 + \gamma)\alpha d \tag{11a}$$

Similarly, for I_b we have

$$\frac{I_b}{I_0} = 1 + (1 + \gamma_e)\alpha_e d \tag{11b}$$
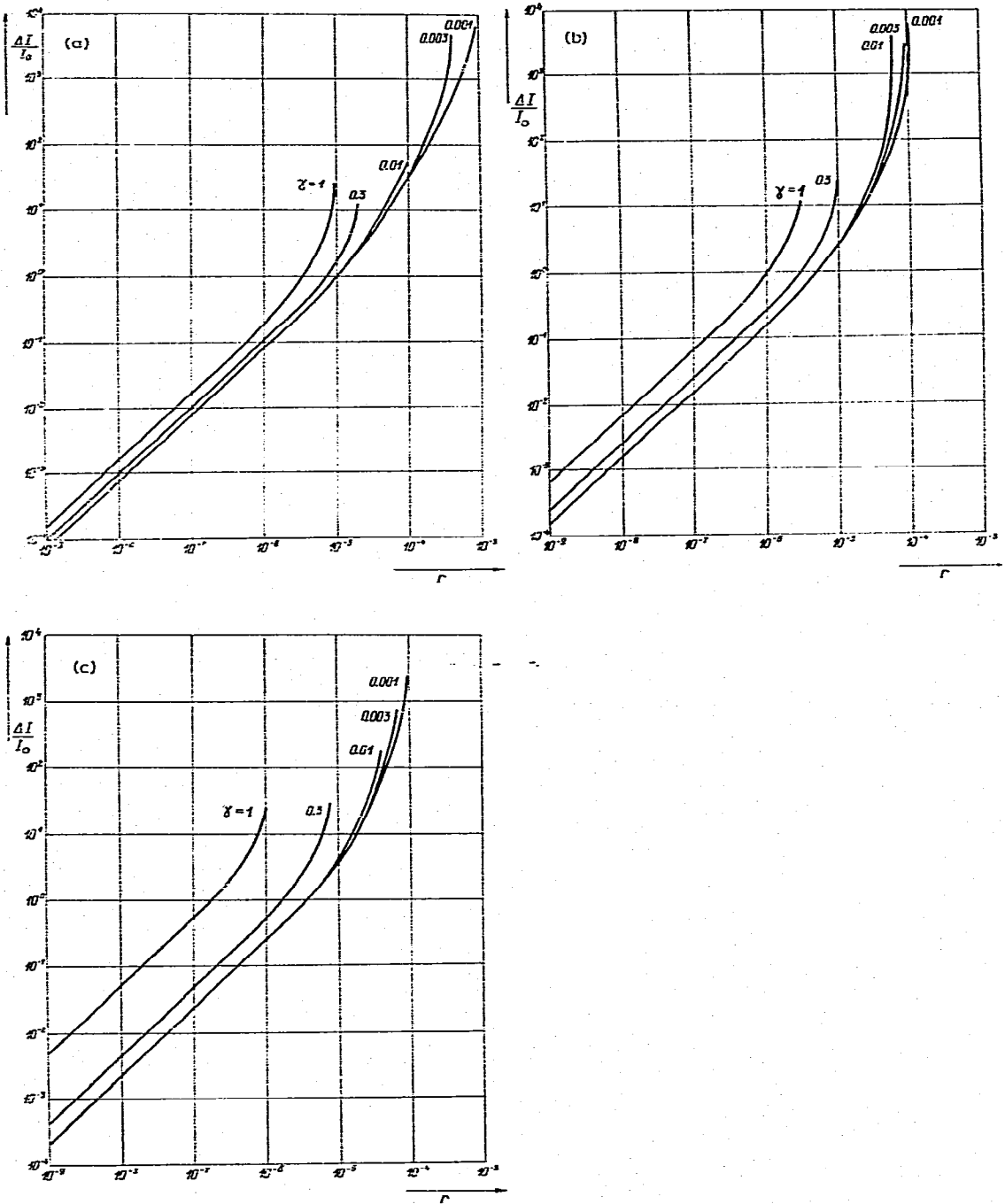
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* The American billion (10^9) is meant.

Fig. 1. Computed variation of the relative current increase of helium detector with the fractional concentration of nitrogen molecules. E/p: a, 4; b, 5; c, 6 V/cm·torr.

Finally, we obtain

$$\frac{I - I_b}{I_0} = (1 + \gamma)\theta \, d \, P \tag{12}$$

under the condition that

$$\gamma = \gamma_e \tag{13}$$

It is obvious that if γ is small and even equal to the values obtained by Dutton and Rees[23], then one can write

$$\frac{I - I_b}{I_0} = \frac{\Delta I}{I_0} = \theta \, d \, P \tag{14}$$

without introducing an error of more than 5%. Taking into account eqns. 5 and 6 and remembering that for atmospheric pressure ($N = 2.7 \cdot 10^{19}$ cm^{-3})

$$A < BN \tag{15}$$

and

$$rQr < BN \tag{16}$$

for concentrations up to $r = 10^{-5}$, for both the singlet and triplet states we have

$$P_s = \frac{rQ_s r}{B_1 N} \tag{17}$$

and

$$P_t = \frac{rQ_t r}{B_2 N} \tag{18}$$

Because Q_s and Q_t are of the same order of magnitude and B_2 is nearly two orders of magnitude less than B_1, we can assume that

$$P = f_t \cdot \frac{Q_t r}{B_2 N} \cdot r \tag{19}$$

Inserting eqn. 19 into eqn. 14, we obtain a linear dependence of the relative current increase with the impurity concentration, r:

$$\frac{\Delta I}{I_0} = \frac{\theta f_t \, d \, r \, Q_t}{B_2 N} \cdot r \tag{20}$$

Of all the terms that have to be found in eqn. 20, only θ has not yet been measured in the range of E/p considered here but has only been calculated theoretically by Hughes[19]. If eqn. 20 is valid, the helium detector should enable θ to be determined experimentally.

Under the same conditions, it should be possible to use the helium detector as an additional method for measuring the cross-section for the Penning effect, supplementing the usual flowing afterglow technique and the thermal energy atomic beam method used previously. Curves analogous to those given by Hartman and

Dimick[8] and shown in Fig. 2 could be used for this purpose, but for an absolute calculation $\Delta I/I_0$ must be plotted on the ordinate. The same plots as those of Hartman and Dimick[8] were made by Poy and Verga[7] for H_2, N_2, Ar, O_2, CO, CH_4, H_2S, CO_2 and by Castello and Munari[32] for H_2, N_2, O_2, CO, CH_4, C_2H_6, C_2H_4, C_2H_2, NO–NO$_2$. H_2S, C_2HF_3, C_2F_4, SO_2 and CO_2.
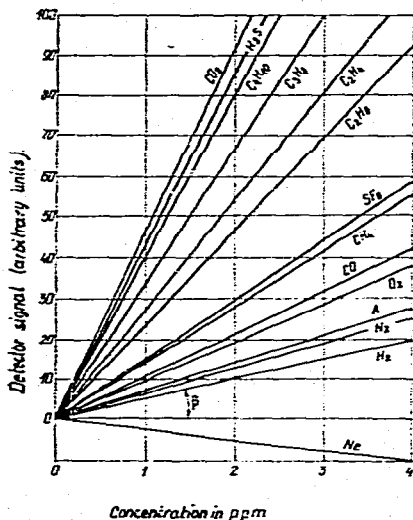

Fig. 2. Effect of gas sample concentration on the helium detector signal by Hartman and Dimick[8]

Attempts at verification

If the derived dependence of the increase in the relative current on extraneous gas concentration in helium is valid, the tangent of the angle of slope. β. of the curves in Fig. 2 should be proportional to the rate constant for the Penning effect, *i.e.* the product of the relative velocity, v, and the cross-section. Q_t. The values of tg β obtained on the basis of the measurements of Hartman and Dimick[8] and the rate constant for the Penning effect. $k_t = v \cdot Q_t$ for triplet states, taken from the paper of Schmeltekopf and Fehsenfeld[22], are given in Table II. In the last column of Table II. the ratio of $k_t/\text{tg } \beta = x$ is given for all of the compounds considered. If the mean value of x is calculated with the exception of H_2, O_2 and SF_6, we obtain

$$\bar{x} = \frac{\bar{k}_t}{\text{tg } \beta} = 21 \cdot 10^{-11} \text{ cm}^3/\text{sec} \tag{21}$$

Evidently, this value is strictly connected with the scale accepted by Hartman and Dimick[8] on both axes of Fig. 2. Schmeltekopf and Fehsenfeld[22] estimated the error of their results to be less than 30%. Assuming that the error of the evaluation of tg β can be neglected in comparison with the error of determining k_t, it is possible to accept that the error of $\bar{x}$ is less than 30%. The values of x for H_2, O_2, SF_6 deviate from the mean value by more than 30%. For O_2 and SF_6, x is about twice the mean value. *i.e.*, the sensitivity of the helium detector is a factor of two lower than that expected from the cross-section for the Penning effect.

TABLE II

SENSITIVITY OF THE HELIUM DETECTOR BY HARTMAN AND DIMICK[8], RATE CONSTANTS FOR THE PENNING EFFECT ACCORDING TO SCHMELTEKOPF AND FEHSENFELD[22] AND THE RATIO OF THESE TWO COEFFICIENTS FOR CERTAIN COMPOUNDS

Compound	Sensitivity of helium detector $(tg\ \beta)$	Rate constant of Penning effect for He (2^3S_1) $(k_t) \times 10^{-11}$ (cm^3/sec)	$k_t/tg\ \beta$ $\times 10^{-11}$ (cm^3/sec)
H_2	0.25	3.18	12.7
N_2	0.313	6.96	22.2
Ar	0.344	7.04	20.5
O_2	0.470	21.0	44.7
CO	0.530	9.85	18.6
CH_4	0.687	13.7	20.0
SF_6	0.72	26.2	36.4
C_2H_6	1.156	25.0	21.5
C_2H_4	1.345	—	—
C_3H_8	1.655	31.7	19.2
C_4H_{10}	2.00	41.7	20.9
H_2S	2.15	—	—
CO_2	2.28	57.5	25.2

Remembering that O_2 and SF_6 are strongly electronegative compounds, it can be considered that it is recombination phenomena that play an important role in this case. Although the cross-section for electron capture in the first peak for SF_6 is $5.7 \cdot 10^{-16}$ cm², which is much greater than that for O_2 ($0.022 \cdot 10^{-16}$ cm²) because of the appearance of the maximum for O_2 at 6.8 eV and at about 0 eV for SF_6 (ref. 33), it seems that recombination weakens the helium detector signal to a greater extent for O_2 than for SF_6.

In the case of H_2, x is about half of the mean value, i.e., ionization is enhanced by some supplementary process other than the Penning effect between triplet metastable states of He and H_2. It should be pointed out that Hasted[34] quoted as many as four different values of the cross-sections for the Penning effect between H_2 and He (2^3S_1), namely 6.1, 1.7, 2.6 and $2.4 \cdot 10^{-16}$ cm², while the value taken for calculations is $1.47 \cdot 10^{-16}$ cm².

Now, it is possible to attempt to give the rate constant coefficient for the Penning effect between He (2^3S_1) and H_2S and C_2H_4, using the mean value of x:

$$\frac{\bar{k}_t}{\overline{tg\ \beta}} = 21 \cdot 10^{-11} \text{ cm}^3/\text{sec}$$

$$k_t = 28.1 \cdot 10^{-11} \text{ cm}^3/\text{sec for } C_2H_4$$
$$= 45.2 \cdot 10^{-11} \text{ cm}^3/\text{sec for } H_2S.$$

The estimation of errors is difficult as we cannot evaluate the influence of electron capture. We have not succeeded in finding the cross-section of electron capture for C_2H_4, but for H_2S Fayard et al.[35] gave the value $1.8 \cdot 10^{-18}$ cm² as the peak at an energy of 2.2 ± 0.1 eV.

CONCLUSIONS

So far we lack sufficient experimental data for the full verification of the proposed model and derived relationships. However, certain shortcomings of eqn. 20 are already evident:

(1) The equation concerns concentrations up to 10 ppm for N_2 and for those gases for which the cross-section for the Penning effect is higher, e.g., for CO_2 it equals $43 \cdot 10^{-16}$ cm^2 —even only up to about 1 ppm. Although the results of Dennis and Shatting[9] confirm that the limit of dynamic range of the helium detector is in this region, in the measurements of Poy and Verga[7] and Lutz[36] it reached as far as 100 ppm.

(2) The proposed model is absolutely unable to explain the anomalous negative signal of the helium detector.

(3) It provides no reason for adding any impurity to the detector carrier gas.

(4) Taking into account that the cross-section for the Penning effect is larger for O_2 than for CO, the model does not explain why the detector sensitivity is higher for CO than for O_2. The same situation arises for SF_6 and C_2H_6.

(5) During the calculation of the rate constant of the Penning effect, the cross-section is multiplied by the mean relative velocity of the helium atom and the extraneous gas molecule. At present, this is the only method as we do not know the dependence of the cross-section on the relative energies of the particles involved.

(6) When P (the probability of the destruction of a metastable atom) was calculated, the following two processes were not taken into account:

$$He^m - He^m --- He + He^+ + e$$
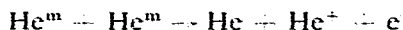
and the Hornbeck–Molnar effect:

$$He + He^m --- He_2^+ + e$$

although the cross-section for the first phenomenon is $100 \cdot 10^{-16}$ cm^2 for triplet states[34].

(7) The proposed model does not take recombination processes into account. They counteract the prompt growth of the current and perhaps if they were considered eqn. 20 could be extended to larger concentrations and provide an explanation of the phenomena mentioned under paragraph (4). On the other hand, it is recombination that might be expected to lead to an explanation of the negative helium detector signal. It is known that the addition of neon to helium results in the domination of the $HeNe^+$ ion[10,37], and the same situation might arise in the case of other impurities. Such complex molecules can have a higher recombination coefficient, show a certain electron affinity, and create negative ions and hence determine the decrease in detector current. However, there are some questions t   answered, namely, does it really happen and to what extent do impurity gas con   ition, electric field, electrode material or other admixtures in helium have a cal. .ic influence on the process of the creation of complex molecules? The inclusion of the recombination can also result in a different temperature dependence of the detector signal being obtained.

(8) The accepted model does not take into consideration helium metastable molecules, He_2^m ($2^3\Sigma$), with energy of about 15 eV (ref. 38). Penning ionization by resonance states and interaction between resonance and metastable states[39,40].

To summarize, the proposed model is not complete and does not elucidate all phenomena, but in a certain range it can be very useful. Other investigations are still necessary in order to clarify the detector mechanism, concerning the characteristics of the detector alone, as well as measurements of the cross-section for processes that can take place within it.

The helium detector should prove to be a useful tool for measuring θ and the cross-section for the Penning effect.

ACKNOWLEDGEMENTS

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