

## On the Partial Liquefaction of Gas Mixture in a Proportional Counter Cooled at Low Temperatures

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The partial liquefaction of filling gas mixtures, which limits the operation of proportional counters at low temperatures, has been discussed with a simple theoretical treatment for the total pressure of two-component-mixtures with gas and liquid phases. The total pressure at 77.3 K as a function of the concentration of components has been calculated for Ar/CH<sub>4</sub>, Ar/CO, Kr/CH<sub>4</sub>, Kr/CO and Ar/Kr mixtures.

KEY WORDS: Proportional Counter/ Low Temperature/ Partial Liquefaction

### 1. INTRODUCTION

The proportional counter is widely used in the Mössbauer spectroscopy, X-ray spectroscopy and others in order to detect low-energy electrons or X rays. Since the operation of proportional counter is based on electric discharges in gas initiated by nuclear radiations, there are some serious difficulties in fabricating the counter which works well at low and high temperatures and applying it to measurements of special purposes, e.g., the resonance electron Mössbauer spectroscopy at high temperatures ( $\leq 1200$  K)<sup>1)</sup> as well as low temperatures ( $\geq 77.3$  K).<sup>2)</sup>

When a gas-filled counter is operated at low temperatures, one of the problems is the partial liquefaction of filled gas which decreases the gas density in the counter, as shown in our previous works.<sup>3,4)</sup> The decrease of the gas density usually results in increasing the gas multiplication in the proportional operation of the counter. In order to avoid the liquefaction, the amount of gas mixture filled in the counter at room temperature ( $\sim 300$  K) should be less than an certain amount corresponding to the saturated vapour pressure (SVP) at a low temperature to operate the counter. The SVP for some pure substances is shown in Fig. 1. As an example, let us consider the case of He/CH<sub>4</sub> mixture. Since the SVP of pure helium at liquid nitrogen temperature (77.3 K) is much higher than that of pure methane (9.3 Torr), the SVP of methane in the mixture is equal to that of pure methane. Then, the maximum partial pressure of methane not to be liquefied at 77.3 K is estimated to be 36 Torr at  $\sim 300$  K according to the equation of state for the ideal gas. However, the case of Ar/CH<sub>4</sub> is not so simple. The equilibrium between gas and liquid phases of the two-component system is to be taken into account, because the difference between the SVP of argon (203 Torr) and that of methane is not so large.

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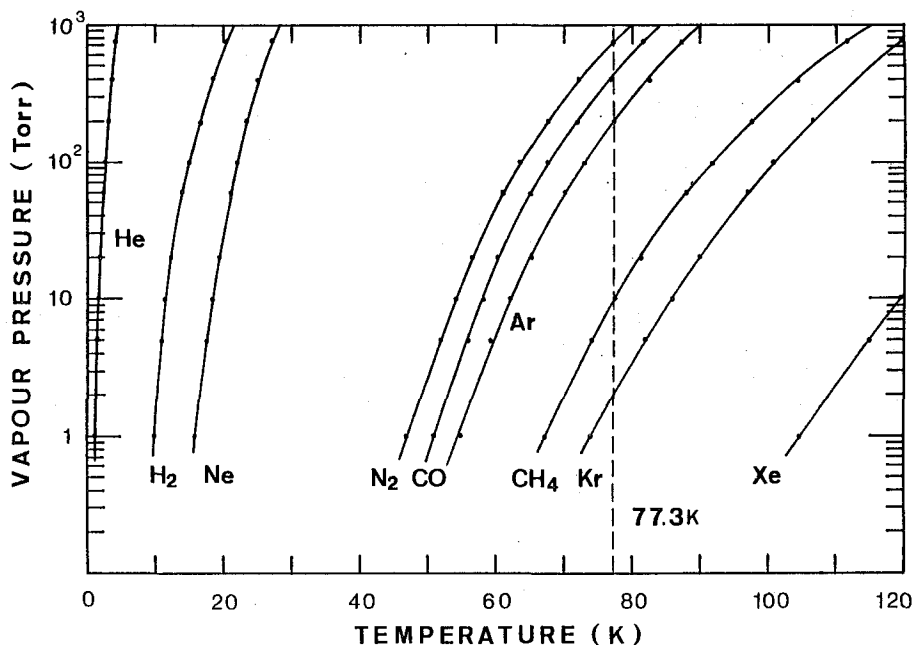


Fig. 1. Saturated vapour pressures of substances useful as counter gases at low temperatures (0–120 K).

In this paper, the total pressure of gas mixtures as a function of temperature and concentration of individual element is deduced in the model of ideal gas and liquid. This is necessary to design proportional counters with gas mixtures such as Ar/CH<sub>4</sub>, Ar/CO, Kr/CH<sub>4</sub>, Kr/CO and Ar/Kr cooled at low temperatures.

## 2. TOTAL PRESSURE OF GAS MIXTURE WITH TWO COMPONENTS

### 2.1. Notations

$p_i$ : partial pressure of a component  $i$  ( $i=1, 2$ ) in the gas phase.

$P$ : total pressure of the mixture cooled at a low temperature  $T$ ,

$$P = p_1 + p_2. \quad (1)$$

$P_o$ : total pressure of the gas mixture filled at room temperature  $T_o$  ( $\sim 300$  K).

$\hat{P}$ : total pressure at a low temperature  $T$  in the model of the ideal gas with a single component,

$$\hat{P} \equiv T P_o / T_o. \quad (2)$$

$p_i^*$ : saturated vapour pressure (SVP) of a component  $i$  ( $i=1, 2$ ) at a low temperature  $T$ .

$\varepsilon_i$ : mole fraction of a component  $i$  ( $i=1, 2$ ) in the gas mixture filled at room temperature  $T_o$ ,

$$\varepsilon_1 + \varepsilon_2 = 1. \quad (3)$$

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$x_i$ : mole fraction of a component  $i$  ( $i=1, 2$ ) in the liquid phase of the mixture cooled at a low temperature  $T$ ,

$$x_1 + x_2 = 1. \quad (4)$$

$x'_i$ : mole fraction of a component  $i$  ( $i=1, 2$ ) in the gas phase of the mixture cooled at a low temperature  $T$ ,

$$x'_1 + x'_2 = 1. \quad (5)$$

### 2.2. Theoretical treatment

When a mixture with two components is separated into gas and liquid phases at a low temperature, the partial pressure  $p_i$  is expressed by

$$p_i = p_i^* x_i, \quad (6)$$

or

$$p_i = P x_i. \quad (7)$$

The equation (6) is known as Raoult's law.<sup>5)</sup> This holds good only for the ideal solution in which the interactions between any combination of components, i.e., (1, 1), (1, 2) and (2, 2), are equivalent each other. In Eq. (7), the gas phase is assumed to follow the equation of state for the ideal gas.

The total pressure as a function of the mole fractions in the liquid phase is called the liquid-phase line,

$$P_L = p_1^* x_1 + p_2^* x_2, \quad (8)$$

which corresponds to the saturated vapour pressure (SVP) of the mixture. The total pressure as a function of the mole fractions in the gas phase is deduced from eqs. (1), (6) and (7) as

$$P_G = p_1^* p_2^* / (p_1^* x'_2 + p_2^* x'_1). \quad (9)$$

This is called the gas-phase curve. When the mixture is not separated into gas and liquid phases at a low temperature  $T$ , its pressure becomes  $\hat{P}$  given by Eq. (2). The mixture remains in a gaseous state when  $\hat{P} \leq p_1^*$  where  $p_2^*$  is defined to be larger than  $p_1^*$ . When  $\hat{P} \geq p_2^*$ , the mixture is always separated into the gas and the liquid phases. When  $p_2^* \geq \hat{P} \geq p_1^*$ , the state of the mixture depends on the relation between  $\hat{P}$  and  $P_G$ : the mixture is partially liquefied if  $\hat{P} \geq P_G$  and remains in a gaseous state if  $\hat{P} \leq P_G$ .

The total pressure of the mixture with gas and liquid phases are deduced as below. The equation of state for the mixture with a volume  $v_o$  and the total mole  $n_o$  at room temperature  $T_o$  is

$$P_o v_o = n_o R T_o. \quad (10)$$

The equation at a low temperature  $T$  becomes

$$P v = n_c R T, \quad (11)$$

where  $v$  is the volume of the gas phase at the low temperature which is given by

$$v = v_o - (A_1 x_1 / d_1 + A_2 x_2 / d_2) n_L. \quad (12)$$

In the above equations,  $R$  is the gas constant,  $A_i$  ( $i=1, 2$ ) is the molecular weight of the component  $i$ ,  $d_i$  is its density in the liquid phase,  $n_G$  and  $n_L$  are the total moles of the gas and the liquid phases at  $T$ , respectively, and

$$n_o = n_G + n_L. \quad (13)$$

The conservation of the component  $i$  is expressed by

$$\varepsilon_i n_o = x_i n_G + x_i n_L \quad (i=1, 2). \quad (14)$$

Using Eqs. (1)–(7) and (10)–(14), we obtain a quadratic equation to deduce the total pressure  $P$  at  $T$ :

$$P^2 - (p_1^* + p_2^* + \hat{P}) \cdot P + p_1^* p_2^* + \varepsilon_1 p_1^* P + \varepsilon_2 p_2^* P - \Delta (P - P_G) (P - P_V) = 0, \quad (15)$$

where

$$\Delta = P_o / (RT_o) (d_1 A_2 - d_2 A_1) / (d_1 d_2) (x_1 p_2^* + x_2 p_1^*) / (p_2^* - p_1^*), \quad (16)$$

$$P_V = (p_2^* d_2 / A_2 - p_1^* d_1 / A_1) / (d_2 - d_1). \quad (17)$$

When  $P = \hat{P}$  in Eq. (15), we obtain

$$(\hat{P} - P_G) \cdot (\Delta P - \varepsilon_2 p_2^* - \varepsilon_1 p_1^* + P_V) = 0, \quad (18)$$

which means that the pressure deduced from Eq. (15) generally goes across the gas-phase line at  $\hat{P} = P_G$ . The factor  $\Delta$  expresses a contribution of the volume of the liquid phase at  $T$  to the total pressure  $P$ . In the region of our interest, i.e.,  $P_o \leq 760$  Torr, the volume effect can be completely ignored; for example, Ar + 10% CH<sub>4</sub> with  $P_o = 760$  Torr has a value of

$$\Delta \cong 6.1 \times 10^{-5}, \quad (19)$$

where  $d_1 = 0.415$  g/cm<sup>3</sup>,  $d_2 = 1.39$  g/cm<sup>3</sup>,  $p_1^* = 9.3$  Torr and  $p_2^* = 203$  Torr are used in the estimation.

The total pressure of a mixture with two components is expressed as

$$P = \hat{P} (\equiv TP_o / T_o) \quad \text{if } \hat{P} \leq P_G, \quad (20)$$

$$P = \frac{1}{2} (p_1^* + p_2^* + \hat{P}) - \frac{1}{2} \sqrt{(p_2^* - p_1^* - \hat{P})^2 + 4\varepsilon_1 (p_2^* - p_1^*) \hat{P}} \quad \text{if } P_G \leq \hat{P} \leq P_L, \quad (21)$$

$$P = P_L \quad \text{if } \hat{P} \leq P_L. \quad (22)$$

The mole fractions  $x_1$ ,  $x_2$ ,  $x_1'$  and  $x_2'$  are

$$x_1 = (p_2^* - P) / (p_2^* - p_1^*), \quad (23)$$

$$x_2 = (P - p_1^*) / (p_2^* - p_1^*), \quad (24)$$

$$x_1' = (p_1^* / P) (p_2^* - P) / (p_2^* - p_1^*), \quad (25)$$

$$x_2' = (p_2^* / P) (P - p_1^*) / (p_2^* - p_1^*). \quad (26)$$

The fraction of the total moles as a sum of components 1 and 2 in the gas phase is given by  $P/\hat{P}$ , while the fraction in the liquid phase is  $(\hat{P}-P)/\hat{P}$ . Then the fraction of the component 1 in the gas phase is expressed by

$$\delta_{G1} = (P/\hat{P})x_1' = (p_1^*/\hat{P})(p_2^* - P)/(p_2^* - p_1^*). \quad (27)$$

The fraction in the liquid phase is

$$\delta_{L1} = (\hat{P}-P)x_1/\hat{P} = (\hat{P}-P)/\hat{P} \cdot (p_2^* - P)/(p_2^* - p_1^*). \quad (28)$$

The fraction of the component 2 in the gas and liquid phases are similarly given by

$$\delta_{G2} = (P/\hat{P})x_2' = (p_2^*/\hat{P})(P - p_1^*)/(p_2^* - p_1^*) \quad \text{and} \quad (29)$$

$$\delta_{L2} = (\hat{P}-P)x_2/\hat{P} = (\hat{P}-P)/\hat{P} \cdot (P - p_1^*)/(p_2^* - p_1^*). \quad (30)$$

### 2.3. Calculated results

As seen in Eqs. (20)–(22), the total pressure at a low temperature  $T$  is a function of the pressure  $P_o$  and the mole fraction  $\epsilon_1$  at room temperature. In Fig. 2, the  $P$ - $\epsilon$  curves of Ar/CH<sub>4</sub> at  $T=77.3$  K are given for  $P_o=760, 380$  and  $190$  Torr. When  $\hat{P}(\equiv TP_o/T_o) \geq P_G$ , the mixture is separated into gas and liquid phases. Then, the mole fractions in gas and liquid phases,  $x_i'$  and  $x_i$ , are different from those of the mixture filled at room temperature  $\epsilon_i$ , while the pressure of the gas phase is equal to that of the liquid phase. As seen in Fig. 2,  $x_i'$  corresponds to the fraction on the gas-phase curve  $P=P_G$  which gives the same pressure as  $\epsilon_i$  does on the  $P$ - $\epsilon$  curve. Rigorous values

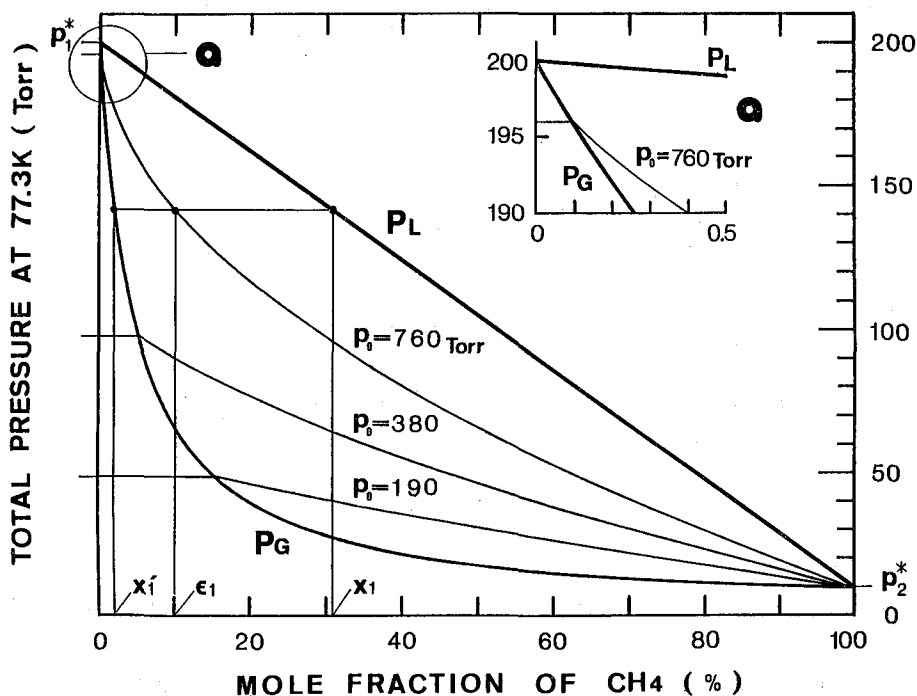


Fig. 2. Total pressure of Ar/CH<sub>4</sub> at 77.3 K as a function of the mole fraction of methane.

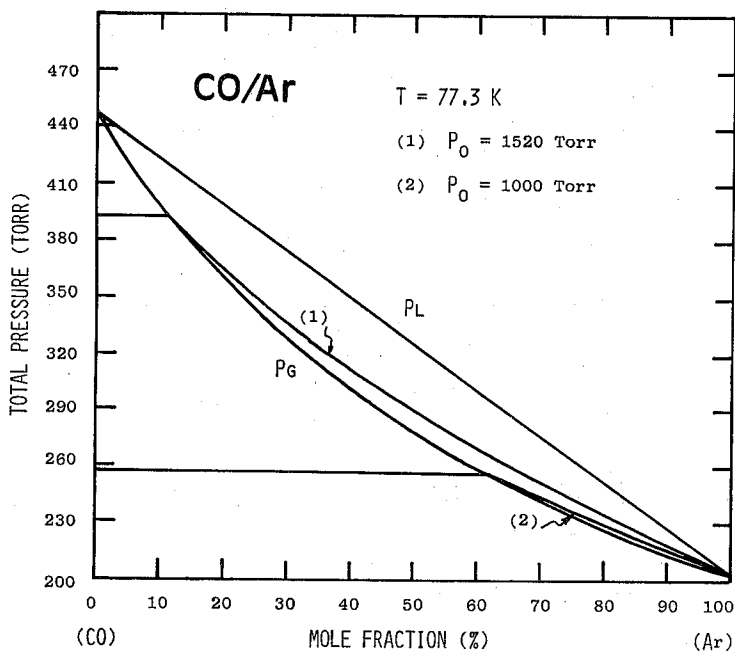


Fig. 3. Total pressure of Ar/CO at 77.3 K as a function of the mole fraction of argon.

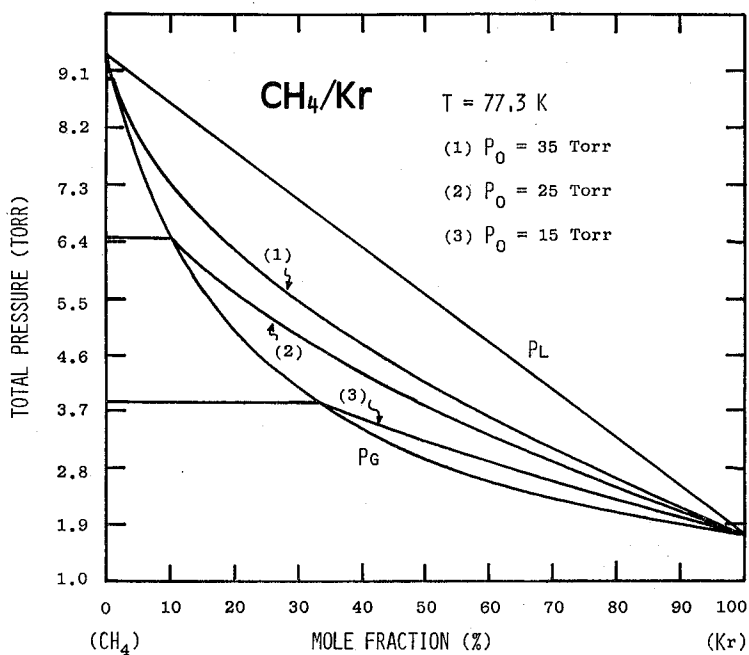


Fig. 4. Total pressure of Kr/CH<sub>4</sub> at 77.3 K as a function of the mole fraction of krypton.

of  $x'_i$  and  $x_i$  can be calculated with Eqs. (23)–(26). Some other results for the  $P$ - $\epsilon$  curves at 77.3 K are given in Fig. 3 (Ar/CO), Fig. 4 (Kr/CH<sub>4</sub>), Fig. 5 (Kr/CO) and

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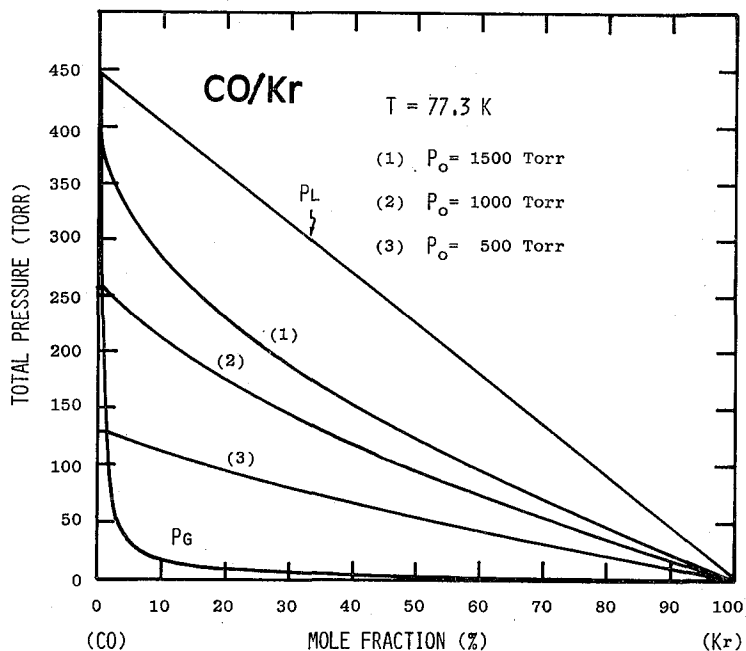


Fig. 5. Total pressure of Kr/CO at 77.3 K as a function of the mole fraction of krypton.

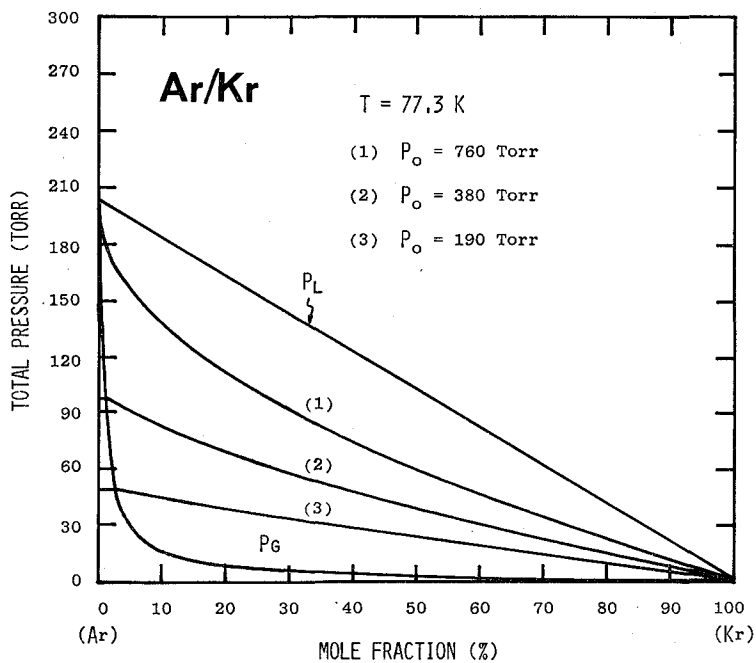


Fig. 6. Total pressure of Ar/Kr at 77.3 K as a function of the mole fraction of krypton.

Fig. 6 (Ar/Kr).

3. GAS MULTIPLICATION FACTOR OF Ar/CH<sub>4</sub>

The gas multiplication factors  $M(V)$  for the Ar/CH<sub>4</sub> mixtures with various CH<sub>4</sub> concentrations (2, 4 and 10%) were measured at  $\sim 300$  and 77.3 K as a function of the anode voltage  $V$ . The filled pressure was 760 Torr, i.e.,  $P_0 = 760$  Torr. A cylindrical proportional counter specially designed for measurements at low temperatures was used<sup>9</sup>; the sensitive volume is 5 cm diam.  $\times$  15 cm length and the anode is made of 40  $\mu$ m diam. tungsten wire. The counter assembly can be directly immersed into liquid nitrogen to cool the counter. Nuclear radiations used for the measurements are 5.9-keV Mn  $K$  X rays from <sup>55</sup>Fe and 5.3-MeV  $\alpha$  particles from <sup>210</sup>Po. The mixture of Ar+10%CH<sub>4</sub> is usually called PR gas, which is commercially available. The  $M(V)$  curve for PR gas at  $\sim 300$  K was determined by two different methods; the values in  $1 \leq M(V) \leq 100$  were obtained by the  $\alpha$ -ray measurement with the <sup>210</sup>Po source, while those in  $40 \leq M(V) \leq 10^4$  were obtained by the X-ray measurement with the <sup>55</sup>Fe source. Both  $M(V)$  curves agree well each other in the region of  $40 \leq M(V) \leq 100$ . As seen in Fig. 7, the multiplication factor  $M(V)$  for all the CH<sub>4</sub> concentrations increases at 77.3 K, indicating that they are separated into gas and liquid phases at this temperature. This is clearly shown in Fig. 2; all the points on the  $P$ - $\epsilon$  curve which correspond to the present experimental conditions, i.e., (760 Torr,  $\epsilon_1 = 2\%$ ), (760 Torr, 4%) and (760 Torr, 10%), are in the area between the liquid-phase line  $P_L$  and the gas-phase curve  $P_G$ . The mole fractions of Ar and CH<sub>4</sub> in the gas and liquid phases for the Ar/CH<sub>4</sub> mixtures are calculated with Eqs. (27)–(30). The

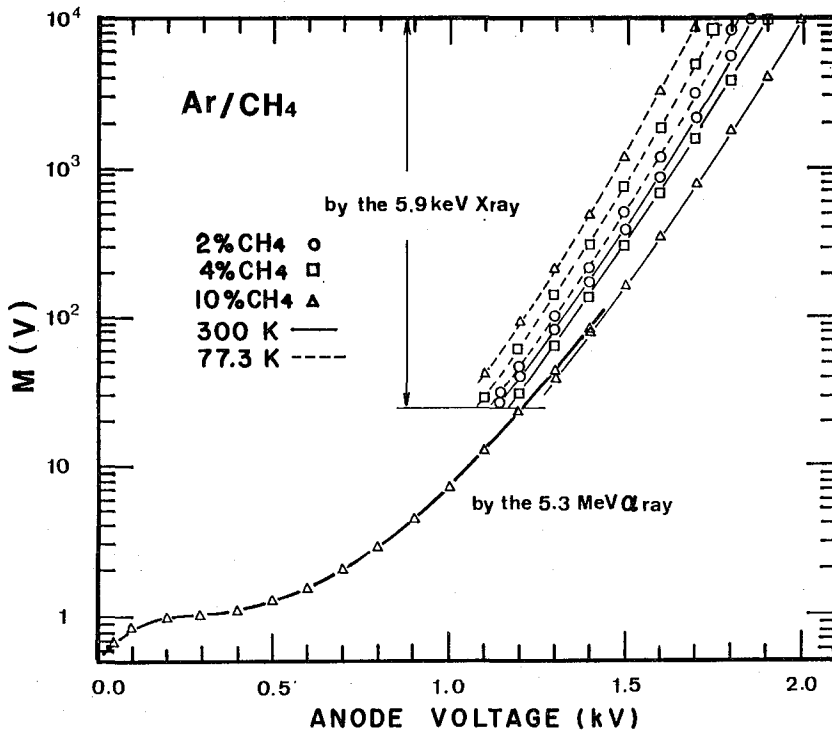


Fig. 7. The gas multiplication factor  $M(V)$  determined for Ar/CH<sub>4</sub> at  $\sim 300$  and 77.3 K.



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Table I. Mole fractions of argon and methane in Ar/CH<sub>4</sub> mixture cooled at 77.3 K

300 K	77.3 K			
	Gas phase		Liquid phase	
	CH <sub>4</sub> (%)	Ar (%)	CH <sub>4</sub> (%)	Ar (%)
2.0	0.6	89.5	1.3	8.6
4.0	0.9	83.4	3.0	12.7
10.0	1.4	71.4	8.3	18.9

results are listed in Table I. When PR gas with  $P_0=760$  Torr is cooled at 77.3 K, the mole fraction of methane in the gas phase changes from 10% to 2%. Then, the ratio of liquid CH<sub>4</sub> to total CH<sub>4</sub> becomes 0.85. This indicates that 85% of methane in PR gas are liquefied at 77.3 K. The same ratio for argon is 0.21. In order to avoid the undesirable increase of gas gain at 77.3 K, the amount of Ar/CH<sub>4</sub> mixture filled in the counter should be so limited that  $P$  given by Eq. (2) is below the gas-phase curve  $P_G$ . For example, when PR gas is used,  $P_0$  must be less than 256 Torr.

### 4. CONCLUDING REMARKS

(i) As seen in Fig. 7, the liquefaction of gas mixtures filled in proportional counters causes the undesirable increase of the gas multiplication factor.

(ii) Gas mixtures available for the operation of proportional counters usually consist of rare gas plus a few percent of polyatomic gas. The polyatomic gas, so called quencher, is necessary to suppress the continuous electric discharge after the ionization of the gas mixture by incident radiations. As seen in Fig. 1, four rare gases (He, Ne, Ar and Kr) are useful in the operation at 77.3 K while there remains only two gases (CH<sub>4</sub> and CO) as quenchers.

(iii) For the detection of low-energy electrons, helium can be used with the quencher of CH<sub>4</sub> or CO. When such mixtures are cooled at 77.3 K, only the quenching gas is partially liquefied if the amount of the gas filled at room temperature exceeds the amount corresponding to the saturated vapour pressure at that temperature. This amount is easily calculated with the equation of state for the ideal gas.

(iv) Ar or Kr is usually used as a main gas for the detection of low-energy X rays. When CH<sub>4</sub> or CO is employed as a quenching gas for the operation at 77.3 K, both the main and the quenching gas may be liquefied. In order to avoid the liquefaction of such mixtures, the amount filled at room temperature should be so limited that the total pressure at 77.3 K may not exceed the gas-phase curve  $P_G$ . The total pressure can be estimated from the theoretical treatment for the two-component system (Sec. 2).

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### REFERENCES

- (1) Y. Isozumi, M. Kurakado and R. Katano, *Rev. Sci. Instrum.*, **52**, 413 (1981).
- (2) Y. Isozumi, M. Kurakado and R. Katano, *Nucl. Instr. and Methods*, **204**, 571 (1983).

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- (3) S. Kishimoto, Y. Isozumi, R. Katano and H. Takekoshi, *Nucl. Instr. and Methods*, in press.
- (4) S. Kishimoto, Y. Isozumi, R. Katano and S. Shimizu, Proceedings on 3rd Internal Symposium on Radiation Physics, Ferrara (Italy), Sept. 30–Oct. 4, 1985.
- (5) W. J. Moore, "Physical Chemistry", 4th ed., Prentice-Hall, (1972).