Nuclear Instruments and Methods in Physics Research A327 (1993) 222–226
North-Holland

NUCLEAR
INSTRUMENTS
& METHODS
IN PHYSICS
RESEARCH
Section A

Present and future production of xenon and krypton in the former USSR region and some physical properties of these gases

P.K. Lebedev
Institute of Nuclear Physics, Novosibirsk, Russian Federation

V.I. Pryanichnikov
"Rosschermet" Corporation, Moscow, Russian Federation

The questions of rare gas handling and production useful for designing large liquid calorimeters of radiation detectors are considered.

1. Introduction

Since the beginning [1] liquid argon, krypton and xenon are considered as very promising media for radiation detectors. At present time the properties of rare gases are quite well known due to works of physicists from USSR, Japan, USA and other countries and allow these gases to be used as active media of large calorimeters for modern detectors. In this case the question of availability of large amounts of the gases and their cost are crucial to implement this idea.

The Novosibirsk INP in cooperation with several factories and the USSR Ministry of Metallurgy has been dealing with the problem since 1984 when we start designing the CMD-2 liquid xenon calorimeter [2] and later in 1986 the liquid krypton calorimeter of KEDR detector [3].

This paper considers the production of xenon and krypton in the former USSR which is one of the main producers of these gases in the world and also regards some physical properties of commercially available gases.

2. Production of xenon and krypton

At present, xenon and krypton are produced as a by-product in giant air separation stations at metallurgical factories. The production rate of oxygen by a typical station is about a billion m^3 per year. There are many such stations in the former USSR, mainly in Russia and in the Ukraine.

Using commonly accepted techniques, most of these stations produce a KrXe mixture containing approximately 93% Kr and only 7% Xe. The pure gases are produced from this KrXe mixture at special separation factories.

The new absorption technology of xenon production from air, developed by the Kryogenmash Association in Moscow [4] has been used for more than a decade in the Kuznetsk factory in Siberia.

In 1991 Ukraine's factories have produced about 11 000 m^3 of KrXe mixture, and similarly the Russia's ones give together with others the total amount of about 25 000 m^3 of mixture containing about 1800 m^3 of xenon. In 1992–1993 the Russian producers are going to increase the production by a factor of 2 and the total production may achieve the level of about 40 000 m^3 of mixture and about 3000 m^3 of xenon. The significant number of oxygen factories are now members of various Joint Ventures including western firms such as Air Liquide, Spectra Gases, AGA Gas etc., selling produced xenon and krypton abroad.

The above data show that the present production level of rare gases is quite sufficient to design large radiation detectors comparable in size with existing liquid argon calorimeters.

The quality of the gases produced by main suppliers in comparison with the state quality standard demands are listed in table 1.

As seen in table 1 practically all producers deliver the gases with an impurity level of one ppm for all admixtures under control. The purest gas is produced by the Balashiha factory near Moscow which began to separate KrXe mixtures in 1992. The Kuznetsk gas needs further purification.

The present prices for krypton gas is on the level of 20–40 Rubles per liter gas and are close, as we know, to the western prices. The xenon price is naturally ten times higher. The prices for these gases have decreased

Elsevier Science Publishers B.V.

Table 1
The purity of Xe and Kr gas produced by different factories

Ukraine		Russia		State Quality Standard
Lisichansk	Mariupol	Kuznetsk	Balashiha	
1	1	5	1	$O_2 < 5$ ppm
2–3	1	10	1	$N_2 < 10$ ppm
<1	1	3	1	$CH_4 < 1$ ppm
1	1	2	1	$CO_2 < 1$ ppm
3–4	2–3	2	1	$H_2O < 5$ ppm

abroad about 3–4 times due to the selling of rare gases from Ukraine and Russia, and have gone up more than 20 times inside the former USSR.

3. How to handle commercial gases

To use commercial gases in radiation detectors it is necessary to know their main physical properties such as life time for electrons due to attachment, attenuation length for scintillation light, drift velocity and its dependence on electrical field strength and temperature, level of radioactivity of krypton due to ^{85}Kr isotope and so on. Naturally, these properties are determined not only by impurities under control but other's as well, therefore, depend on the factory-supplier choice.

Table 2
Attenuation length for commercial liquid Xe and Kr

Factory	Attenuation length L [cm]	
	Xe	Kr
Lisichansk	0.4	4 –6
Mariupol	0.1	1.5–2.5
Kuznetsk	$\ll 0.1$	–

3.1. Attenuation length of electrons

To measure the attenuation length of electrons in a liquid due to attachment we used the "old" well known X-ray technique [5], when a short X-ray beam pulse is injected in a plane ionization chamber from the cathode side and the duration of the current pulse in the chamber allows us to determine the drift velocity but the decrease of pulse amplitude allows to determine lifetime of electrons. The measured values of attenuation length L at 1 kV/cm field strength for commercial gases with 1 ppm oxygen contamination from different suppliers are presented in table 2.

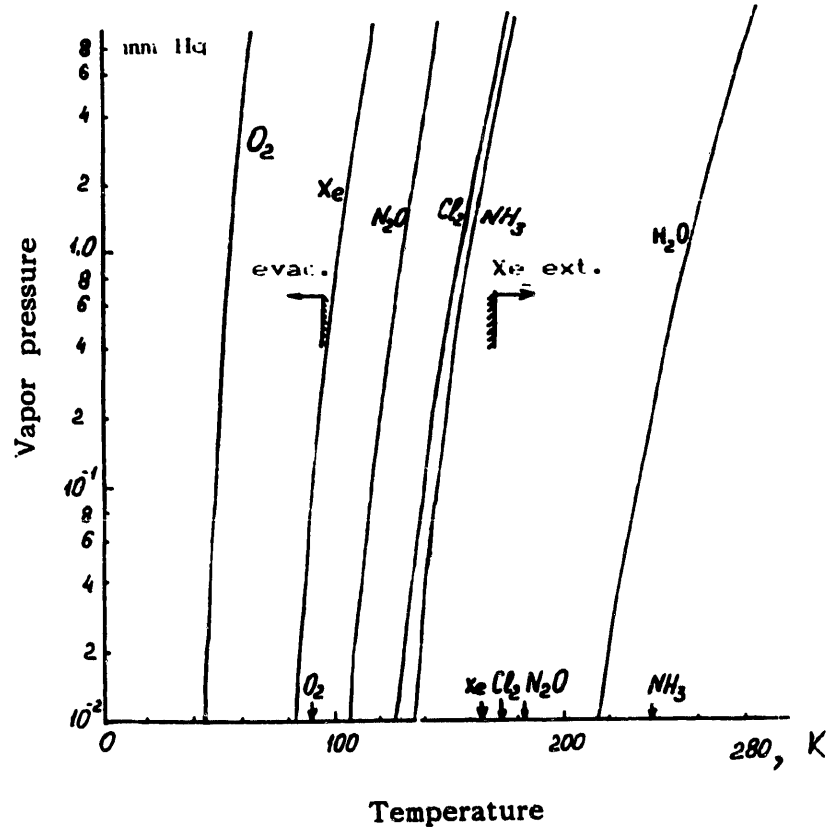

Fig. 1. Vapor pressure dependence vs temperature for xenon and impurities.

As seen the attenuation length in xenon is approximately equal to the predicted valve according to an empirical formula [6]

$$L[\text{cm}] = kE[\text{V/cm}]/p[\text{ppm}],$$

relating impurity concentration p, electrical field strength E and attenuation length L. But in krypton the measured values differs significantly from the prediction obtained under the assumption that the constant k in the formula is the same for liquid xenon and krypton. The more plausible explanation of the fact is that the 1 ppm contamination listed in supplier gas certificates is the upper limit of chromatograph sensitivity and in reality the impurity concentration is lower.

If needed we can make additional purification of gases using the "freezing" impurities method for dirty gas to separate the impurities with boiling points very different from the main gas, the hot calcium reactor or the Ti-discharge method [7].

In the "freezing" impurities method the difference in boiling point temperatures for main gas and for admixtures is used. For example, fig. 1 presents the vapor pressure dependence on temperature for xenon and for admixtures like oxygen, water and other's.

As seen if the cylinder containing xenon is at a temperature lower than Xe boiling point, you can purify it from impurities with lower boiling points by evacuating the vessel. After that, the temperature of the cylinder is set higher than the Xe boiling point and xenon is extracted to another clean cylinder. The impurities with boiling points higher than that of xenon are left frozen in the first cylinder.

This method is effective for dirty gas and allows for example to separate xenon–air mixture with a concentration of air as high as 50% to the level of 10–15 ppm.

To purify the gas to 0.1 ppm level or better, a hot Ca-getter can be used. By passing Lisichansk or Mariupol gas one time through a reactor at 800°C, it is possible to obtain an attenuation length for electrons in liquid xenon equal to 1.5 cm and in liquid krypton up to 10–20 cm. The hot calcium appeares to be a very effective purifier of commercial krypton.

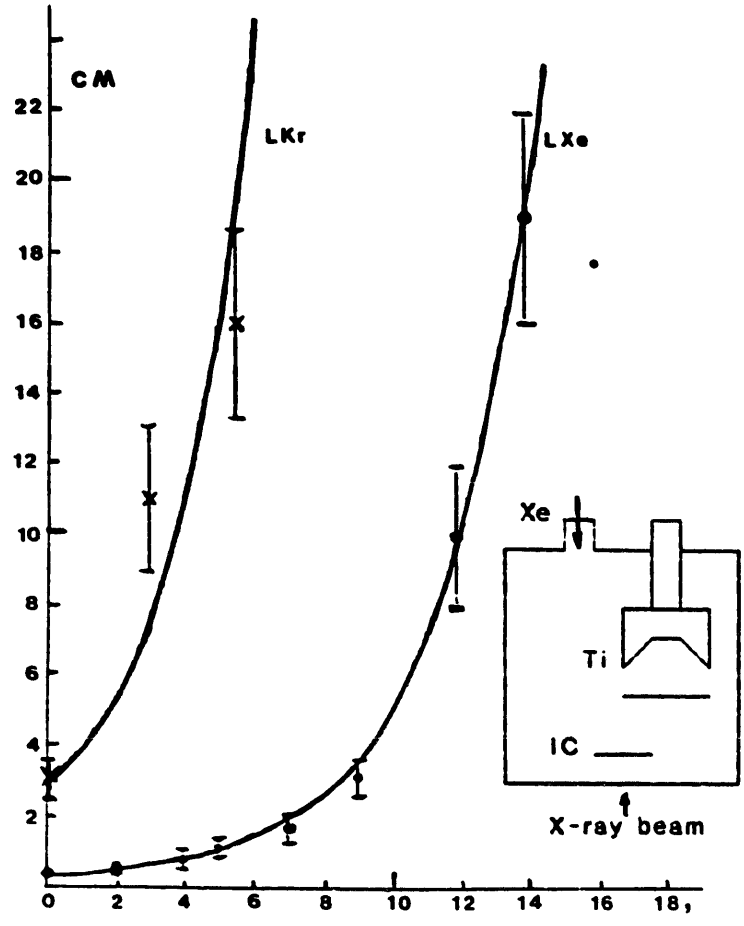

Fig. 2. Time dependence of attenuation length for electrons in liquid xenon and krypton as a function of the operation time of the Ti-discharge device.

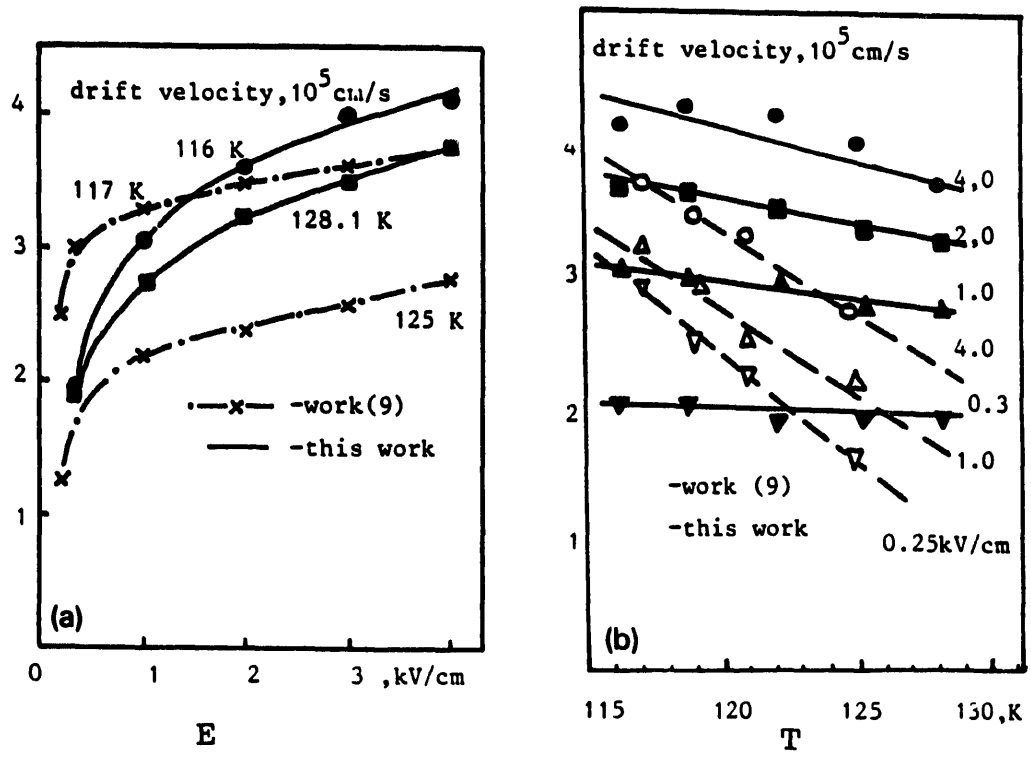

Fig. 3. Drift velocity of electrons in liquid krypton vs (a) electrical field strength and (b) temperature for Mariupol (solid lines) and Lisichansk (dashed) gases.

The Ti-discharge method was used to obtain an attenuation length in liquid xenon up to 20 cm. In this technique metalic titanium is spread in a volume filled by liquid under a spark discharge between Ti-electrodes placed inside the liquid. The rate of purification can be seen in fig. 2. It is practically the same in the xenon and the krypton case.

3.2. Attenuation length for scintillation light

The Bolozdinya's group from ITEPH (Moscow) has measured that the Lisichansk liquid xenon is transparent to the self-scintillation light up to 30 cm, and liquid krypton after purification by the hot calcium getter up to 1–2 m [8].

3.3. Long term gas storage

Our experience shows that it is possible to conserve purified gas having attenuation length for electrons in the liquid equal to $L = 1$–4 cm for about one year without significant deterioration in stainless steel cylinders cleaned inside by benzene, acetone and deionized water and backed in a furnace at the vacuum of about 0.001 mm Hg.

3.4. Krypton radioactivity level

The radioactivity of krypton due to ^{85}Kr isotope with 10.8 y life time and 0.67 MeV beta's is a significant source of noise for calorimeters. The concentration of the isotope can vary due to different time and place of gas production.

Our measurement of radioactivity level of Mariupol krypton produced in the Ukraine after the Chernobil gives 326 decays/s per cm^3 of liquid in good agreement with measurements by ITEPh and KEDR groups made respectively with Lisichansk and Mariupol krypton produced previously.

3.5. Drift velocity dependence on temperature and electrical field strength

Electron drift velocity depends on the concentration of non-electro-negative impurities in liquid which is not generally tested in commercial gases and therefore drift velocity can strongly depend on the factory-suppliers.

Fig. 3 presents results of our measurements of drift velocity as a function of field strength and temperature made for Mariupol krypton in comparison to ITEPH

results [9] dealing with Lisichansk gas. As seen the behavior of velocities in krypton from Mariupol and Lisichansk are significantly different. The most striking difference is the dependence on temperature which is about 5% K^{-1} for ITEPH data and about 0.5% K^{-1} for ours. Our value for krypton is in agreement with measurements for xenon [10] and argon [11].

4. Conclusions

Present production of xenon and, especially, krypton is quite enough to design liquid radiation detectors of size equal to liquid argon calorimeters. The production of the gases is going to double in a year or two. The situation is in favor of foreign physicists as prices go down abroad and go up in the former USSR. The physical properties of the gases significantly depend on the suppliers and must be controlled during the collection of gases for detectors.

References

[1] N. Davidson and A.E. Larsh, Phys. Rev. 74 (1948) 220.
[2] G.A. Aksenov et al. Preprint INP 85-118, Novosibirsk (1985).
[3] V. Anashin et al., Proc. Int. Symp. on Position Detectors in High Energy Physics, Dubna, 1988, p. 58.
[4] V. Vorotinsev, Ph.D. Thesis, Leningrad, 1973.
[5] See, for example, P. Vasiliev et al., Preprint FIAN, 43 (1986).
[6] See, for example, C. Brassard, Nucl. Instr. and Meth. 162 (1979) 29.
[7] S. Pokachalov et al., these Proceedings (Liquid Radiation Detectors), Nucl. Instr. and Meth. A327 (1993) 159.
[8] D. Akimov et al., these Proceedings (Liquid Radiation Detectors), Nucl. Instr. and Meth. A327 (1993) 155.
[9] S. Anisimov et al., Preprint ITEPH, 16, 1984.
[10] T. Doke, Nucl. Instr. and Meth. 196 (1982) 87.
[11] E. Guschin et al., Exp. Meth. Nucl. Phys. 7 (1980) 104.