Вісник ХНУ, № 1158, серія «Фізика», вип. 22, 2015. с. 48-50

PACS 05.70.-a; 05.60.-k
UDC 536.79, 538.93, 53,043

Special features of low temperature gases separation using peltier elements and mixture throttling

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It was examined special features of Peltier elements using for gas mixture separation into components and low temperature cryogenic liquids obtaining in low-powered production using Joule-Thomson effect in the second stage of cooling. It was carried out the measurements of necessary heat, electricity and cooling flows for components separation of the air and hydrogen-oxygen mixtures in order to obtain liquid nitrogen, oxygen and hydrogen with a help of specially made investigation equipment.
Keywords: gas separation by cooling, Peltier element, throttling, liquid nitrogen, oxygen, hydrogen.

Розглянуті особливості використання елементів Пельтьє для розділення суміші газів на компоненти та одержання низькотемпературних кріорідин в малопотужних виробництвах з використанням ефекту Джоуля-Томсона на другому ступені холоду. За допомогою створеного дослідного обладнання проведені вимірювання необхідних потоків тепла, електроенергії та охолоджувача для розділення на компоненти повітря і воднево-кисневої суміші з метою отримання рідких нітрогену, оксигену та гідрогену.
Ключові слова: розділення газів охолодженням, елемент Пельтьє, дроселювання, рідкі нітроген, оксиген, гідроген.

Рассмотрены особенности использования элементов Пельтье для разделения смеси газов на компоненты и получения низкотемпературных криожидкостей в маломощных производствах с использованием эффекта Джоуля-Томсона на второй ступени холода. С помощью созданного исследовательского оборудования проведены измерения необходимых потоков тепла, электроэнергии и хладагента для разделения на компоненты воздуха и водородно-кислородной смеси с целью получения жидких азота, кислорода и водорода.
Ключевые слова: разделение газов охлаждением, элемент Пельтье, дросселирование, жидкие азот, кислород, водород.

One of the main methods [1] of industrial gas separation into components with high purity is low temperature method, based on the using of boiling temperatures differences in the liquid state of different substances, which is caused by the nature of intermolecular interactions [2,3]. Other (non-cryogenic) methods are also often used, for example membrane one, where there are conditions for small size molecules moving through a small hole or cavity fiber, adsorption method (carbon nanotubes are especially promising today [4]), and space division method with a space separation of mixture on electrodes [5]. Last one is used in water electrolysis (Figure 1) when oxygen is evolving at the anode and hydrogen – at the cathode.

This method is more effective using the electrode plates placed in opposite one to another, between which transparent membranes for ions are fixed. Gases evolving at the electrodes go up under Archimedes force to different capacities (figure 1). However, the existing of the membranes and separated capacities for gases withdrawal to different capacities make process of separation more difficult and slower. Therefore, for big capacities, at first the gas mixtures are obtained, and then the separation is caring out, for example, using low temperatures [6].

The aim of this study was to examine the possibility of cryogenic separation of gas mixture into components in low-powered unit using deep cooling process without gas-expansion machines in conditions of limited element base. Low temperatures are easy to get using Peltier semiconductor elements when it is enough low power for heat flow withdrawal [7].These are machineless devices in the form of the plate, one side of which is heating by current and requires heat withdrawal, and another one is cooling. In this case the temperature differences between the surfaces can reach more than 50 K. Peltier elements cascade connection is applied too [8]. During a parallel connection increases the cooler capacity while in sequential case it will be for the temperature difference. These plates using experience proves that in the two-stage sequential connection they can create low temperatures with the

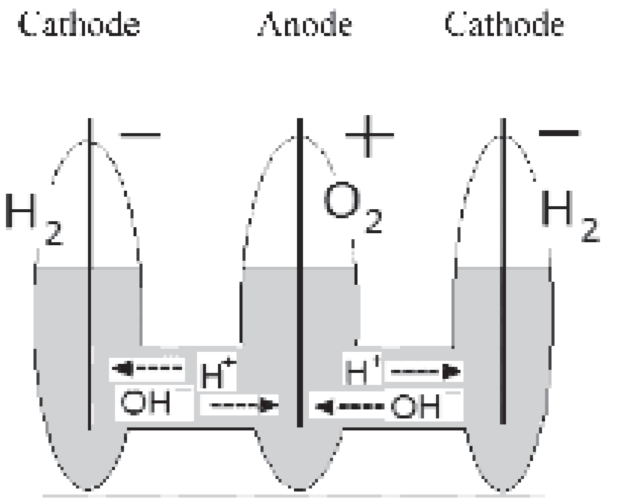

Fig.1. Diagram of non-cryogenic manner of gases separation during water electrolysis without low temperature using in consideration of product stoichiometry (double volume of H_2 for one volume of O_2).

difference of over 100 K and operate in a stable mode.

However, Peltier elements are the most effective under the normal conditions and with a few sequential cascades [8], but lower temperatures obtaining for the accumulation of elements in cascade leads to bigger thermal losses and total thermal resistance of the bridge. There is reduction of unit efficiency at low temperatures. In low-powered scheme, shown in figure 2, Joule-Thomson effect of gas throttling through a porous baffler from 1.5 MPa pressure to atmospheric pressure was applied to further mixture temperature reducing [2]. Because of Peltier elements, the temperature of hydrogen that needed to be cooled was becoming less than inversion temperature. For oxygen it reaches 893 K, and for hydrogen is 204.6 K.

Thus, Peltier elements using two-stage sequential diagram make possible in both cases to get mixture temperature reducing at first stage of cooling. It should be mention that oxygen liquefies at 90.2 K and solidifies at 54.4 K. Hydrogen liquefies at 20.4 K and solidifies at 13.8 K. Therefore, to separate oxygen from nitrogen or hydrogen for Peltier elements with throttling on the second stage is not a technical problem (nitrogen liquefies at temperature of 77.4 C and solidifies at 63.15 K). This process is more complicated for hydrogen. Especially difficult is to liquefy helium as the temperature must be 4.2 K. Helium solidifies only when at 2 K temperature is creating additional 3.76 MPa pressure for the main isotope ^{4}He and for ^{3}He at 1.0 K and 87 MPa [10].

In the diagram (figure 2) was shown the additional temperature reduction and throttling of mixture conducted after using semiconductor elements. The mixture was separated by the pressure expansion from 1.5 MPa to normal one. It was in Dewar vessel. The general scheme of unit was shown in figure 2. Compressed gas mixture for cooling was moving sequentially through two radiators. Then gases reach cold side of Peltier bridge, hot side of which was cooling by running water or gas. Following temperature reducing of gas mixture was in the heat-transfer apparatus, where counter cold flow of gases from Dewar vessels that have been not liquefied during throttling in a cryostat returned to the balloon.

Starting of liquid oxygen selection from the air or detonating mixture could be observed in Dewar translucent glass vessel. Cessation of oxygen accumulation in the vessel indicates its selection completion. Then, in the

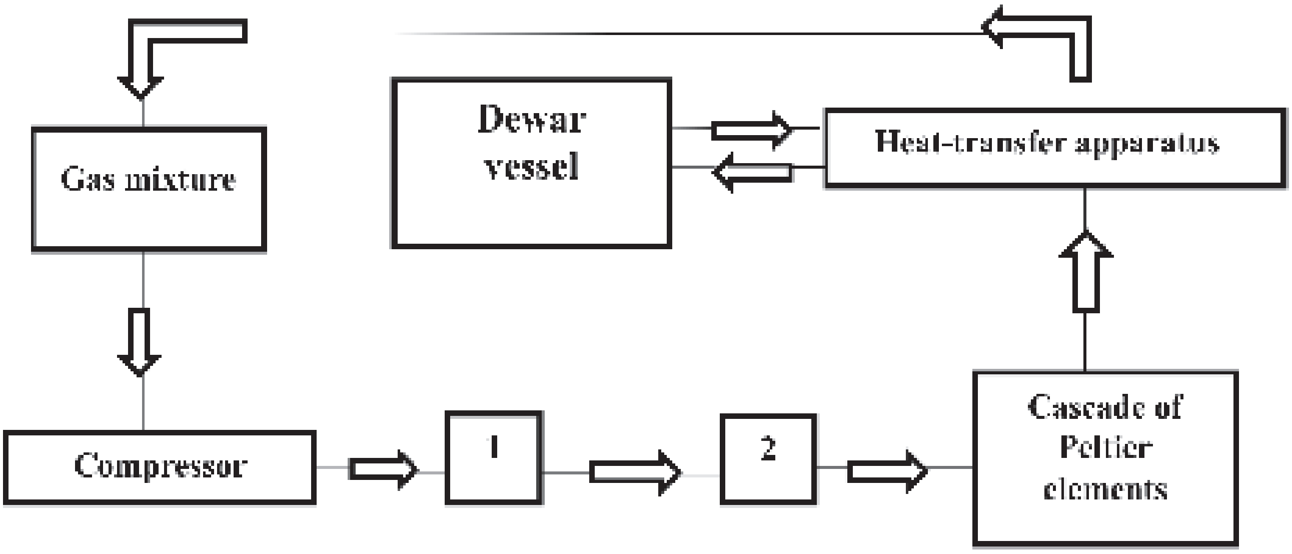

Fig.2. The scheme of low temperature separation of gases from gas mixture: 1 - radiator with air cooling and drier; 2 - radiator with dry or ordinary ice cooling and decarbonifier (water solution of NaOH). It was used Peltier TES1-12706 elements with power 53 V (size 40x40 mm^2). In Dewar translucent glass vessel we can obtain gases mixture separation due to one of the components liquefaction.

first case, nitrogen is extricating with argon in the balloon (argon concentration increases in dozens of times from 1%). If the mixture is detonating it will be undiluted hydrogen. However, some little residual concentration of oxygen remains in the balloon. Table 1 shows the ratio of gas components of air that successively transfer into the liquid during throttling.

Hydrogen in the separation process of detonating mixture begins to liquefy [10] if it has been cooled before throttling by liquid nitrogen or oxygen and if thermal insulation was provided. Getting of liquid hydrogen provides an opportunity to study and to use new application of superconductivity of magnesium diboride MgB_2 (2001, transition into a state of superconductivity occurs at 39 K [11]).We can get liquid helium from liquid hydrogen by throttling without which fundamental low-temperature researches are almost impossible today. Liquid hydrogen is very important today as the most powerful and the most ecological fuel, which is used for solving current problems of energy, environment and materials science [12, 13] and for creation of rocket fuels for near space [14].

As a result of done work with using Peltier semiconductor elements and method of throttling (Joule-Thomson effect) was created a low-powered unit for the air and hydrogen liquefaction, which allowed to conduct low temperature researches and to teach undergraduates and graduate students.

Table 1.

The mean air composition in normal environment conditions.

Components of the air	Concentration by capacity %	Concentration by weight %	List number
Nitrogen	78,2	75,5	[9]
Oxygen	20,9	23,2	[9]
Inert gases	0,9	1,3	[9]

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