CHEMICAL ENGINEERING AND CHEMICAL PROCESS TECHNOLOGY – Vol. II - Refrigeration - D. Mikielewicz, J. Mikielewicz

REFRIGERATION

D. Mikielewicz

Gdańsk University of Technology, Faculty of Mechanical Engineering, Poland

J. Mikielewicz

Institute of Fluid Flow Machinery, Polish Academy of Sciences, Gdańsk, Poland

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Contents

- 1. Introduction
- 2. Methods of refrigeration
- 2.1. Non-cyclic Refrigeration
- 2.2. Cyclic Refrigeration
- 2.2.1. Carnot Cycle
- 2.2.2. Lorenz Cycle
- 2.2.3. Vapor-compression Cycle (VCC) Linde Cycle
- 2.2.2. Vapor Absorption Cycle (VAC)
- 2.2.3. Gas Cycle
- 2.2.4. Thermoelectric Refrigeration
- 2.2.5. Magnetic Refrigeration
- 2.2.6. Vortex Tube
- 2.2.7. Thermoacoustic Refrigeration
- 2.2.8. Steam jet refrigeration (SJR)
- 2.2.9. Metal Hydride refrigeration
- 3. Refrigerants
- 3.1. Azeotropic, near Azeotropic and Zeotropic Mixtures
- 3.1.1. Azeotropic Mixtures
- 3.1.2. Non-azeotropic Mixture
- 3.1.3. Near-azeotropic Mixture
- 3.1.4. Blends
- 3.1.5. Glide
- 3.2. Nomenclature used in Refrigeration Notation
- 3.3. The Greenhouse Effect
- 3.4. The Montreal Protocol
- 4. New developments in refrigeration technology
- Glossary
- Bibliography

Biographical Sketches

Summary

Refrigeration is of importance to many chemical engineering problems. That is to produce and maintain temperature which is lower than the ambient. Since that process can only be produced by the withdrawal of heat and for that reason refrigeration is equivalent to heat removal. Refrigeration has a diverse nature and covers a large number of processes ranging from cooling to air conditioning and from food refrigeration to human comfort. Significant applications can also be found in chemical engineering. In the chapter different ways to achieve lower temperature are described and discussed. Additionally, issues related to working fluids in refrigeration technology have been presented, ranging from their nomenclature, through properties and applicability and finally restrictions in use.

1. Introduction

The problem of refrigeration is to produce and maintain temperature which is lower than the ambient. Since that process can only be produced by the withdrawal of heat and for that reason refrigeration is equivalent to heat removal. Refrigeration has a diverse nature and covers a large number of processes ranging from cooling to air conditioning and from food refrigeration to human comfort. Applications can be found in chemical engineering industry (removal of heat of reaction, heat of mixing, separation of salts, liquefaction of gases), food industry (processing, storage), air-conditioning, ice manufacture, electronics (cooling of high-duty equipment), manufacturing industry (heat treatments, metal cutting), pharmaceutical industry, biomedical applications (blood and tissue storage, hyperthermia in surgery) and finally fundamental research. Applications of refrigeration in the area of food processing and preservation have been given impetus to the economic development of countries producing meat, fruits or vegetables, which are usually located in the warm climate zone, allowing them to export these goods long distances and in that way contributing to the sustainable development of these countries.

Spontaneous transfer of heat from lower to higher temperature is not possible. In order to satisfy the Second Law of Thermodynamics, some form of work must be supplied to the system to accomplish this. Traditionally mechanical work is utilized for that purpose but also other modes of work, such as magnetism, laser or other means can be used. In practice, heat transfer mechanisms considered in refrigeration use the three basic methods, namely convection, conduction and radiation. First attempts to attain low temperatures were through the direct contact with a colder body, namely ice or snow. Later other substances and processes were found suitable for that purpose. In general, the term heat removal refers to any natural or artificial process in which heat is being dissipated. The end process of heat rejection is always dissipation of heat to the atmosphere. A topic is quite complicated due to the fact that thermodynamics, fluid mechanics and heat transfer are always encountered in every refrigeration process or application. The process of artificially producing extremely low temperatures is referred to as cryogenics.

Continuous refrigeration can be achieved by several types of physical phenomena. Effectively any power thermodynamic cycle, when reversed, becomes a refrigeration cycle. A refrigeration device can be used to heat a volume that is at higher temperature then surroundings. In such case the device is called a heat pump. The distinction between a refrigerator and a heat pump lies rather in application to specific situations then in the principle of operation and hence here we will merely concentrate on the refrigeration techniques.

There has always been a need or at least a desire to cool the specific environment below ambient temperatures. Records related to that date back to around 2000 BC and indicate that people knew of the positive preserving effects of colder temperatures on food. The earliest methods of producing cold were based on naturally occurring ice and freezing mixtures such as salt and snow. The records confirm that ancient cultures such as Chinese, Hebrews, Greeks, Romans, Persians had developed capabilities to produce cold. Alexander the Great served his soldiers snow-cooled drinks around 300 BC, and Khalif Madhi, as far back as 755 AD, provided refrigerated transport across the desert to Mecca using snow as a coolant, Koelet (1992). Naturally occurring ice was either shipped from colder climates or collected in the winter and stored in cold houses (icehouses), some of which persisted even to early twentieth century. These houses were made of various insulating materials, such as straw dirt or even manure. Thickness of walls was reaching one meter in some cases.

The fact, that sodium nitrate lowers the temperature of water upon dissolving, was known in the 14th century A.D. In the 16th century, the discovery of chemical refrigeration was one of the first steps toward artificial means of refrigeration. Sodium nitrate or potassium nitrate, when added to water, lowered the water temperature and created a sort of refrigeration bath for cooling substances. In Italy, such a solution was used for example to chill wine. The main method used to generate the refrigeration effect relies on the evaporation of a dedicated liquid. The fact that ether chilled the skin was already known around 1755. By reducing the pressure above the ether, it boils and lowers its temperature to the point that forms the ice. That effect laid grounds for the first half of the refrigeration cycle, the evaporator. For economical reasons, it is however impossible to operate all the time with fresh refrigerant. For technical applications a cyclic process must employed through which the refrigerant passes again and again. The idea of putting condensation and evaporation techniques together to create a cyclic system, as the first cyclic refrigeration machine, was completed by Jacob Perkins in 1834. In 1842, John Gorrie, designed the first system for refrigerating water to produce ice. He also originated the idea of using his refrigeration system to cool the air for comfort in homes and hospitals, i.e. air-conditioning. His system compressed air, then partially cooled the hot compressed air with water before allowing it to expand while doing part of the work required to drive the air compressor. That isentropic expansion cooled the air to a temperature low enough to freeze water and produce ice. Gorrie built a working prototype, but his system can rather be regarded as a commercial failure. It was Alexander Twining who began experimenting with vapor-compression refrigeration in 1848 and obtained patents in 1850 and 1853. He is credited with having initiated commercial refrigeration.

The first gas absorption refrigeration system using gaseous ammonia dissolved in water (referred to as "aqua ammonia") was developed by a Frenchman, Ferdinand Carré in 1859 and patented in 1860. Due to the toxicity of ammonia, such systems were not developed for use in homes, but were used to manufacture ice for sale. Around the world the consumers at that time still used the ice box with ice brought in from commercial suppliers, many of whom were still harvesting ice and storing it in an icehouse. This was not, however, a satisfactory solution since the temperatures achieved were not below +4 to $+2^{\circ}$ C. Another critical issue was a fact that natural ice is not

entirely germ-free and cannot therefore be used without restrictions for the cooling of food. In 1846 Carl von Linde built his first ammonia-compression refrigerator. That paved the way for numerous technical applications of such refrigeration systems. At the same time, considerable efforts were made to design and construct devices for the purpose of withdrawing heat from the surroundings through evaporation of liquids and thus to produce low temperatures.

2. Methods of Refrigeration

2.1. Non-cyclic Refrigeration

In these methods, refrigeration can be accomplished by melting ice or by subliming dry ice. These methods are used for small-scale refrigeration such as in laboratories and workshops, or in portable coolers. Ice owes its effectiveness as a cooling agent to its constant melting point of 0°C as well as availability. Consumable products maintained at this temperature or slightly above have an increased storage life. Solid carbon dioxide, known as dry ice, is used also as a refrigerant. Having no liquid phase at normal atmospheric pressure, it sublimes directly from the solid to vapor phase at a temperature of -78.5°C. Dry ice is effective for maintaining products at low temperatures during the period of sublimation. Its application to chill the sea products during the transport to supermarkets is generally acknowledged by connoisseurs.

2.2. Cyclic Refrigeration

Thermodynamic cycles allow the reciprocal conversion in a continuous manner of thermal energy into other kinds of energy. A work-supplying cycle is referred to as the power cycle. Such cycles are executed in the clockwise direction and they remove heat from the hot reservoir, execute work, and reject heat to the cold reservoir (surroundings). A reversed cycle is executed counter-clockwise and consumes external work in order to cool the cold reservoir by transferring heat to the high temperature reservoir (surroundings), see Fig. 1. Reversed cycles are used to extract heat from bodies colder then the surroundings (cooling effect), referred to as refrigeration cycles, or to heat spaces by extracting heat from low-temperature sources (heating effect), called heat pump cycles.

The efficiency of a cycle is evaluated by the coefficient of performance (COP). In general, the effectiveness of a cycle is the ratio of the desired effect to the cost at which such effect is attained (energy expended). In the case of power cycles, the desired effect is the net work transfer, and the expended energy is the heat extracted from the high-temperature reservoir. In such case the COP is named the efficiency of the cycle, which is always smaller than unity. For the reversed cycles, the desired effect depends on the purpose of the cycle, which is different in case of refrigeration mode and heat pump mode, whereas the energy expense is the same, namely the external work input:

$$COP = \frac{benefit}{cost} \tag{1}$$



Figure 1. Power and reversed cycles.

Cyclic refrigeration constitutes a refrigeration cycle, where heat is removed from a lowtemperature space or source and rejected to a high-temperature sink with the help of external work, and is the inverse sequence of processes found in the thermodynamic power cycle. In the power cycle, heat is supplied from a high-temperature source to the engine, part of the heat being used to produce work and the rest being rejected to a lowtemperature sink. This satisfies the second law of thermodynamics. A refrigeration cycle describes the changes that take place in the refrigerant as it alternately absorbs and rejects heat in the course of its circulation through the refrigerator. It can be applied to heating, ventilation, air conditioning and refrigeration (HVACR) work. The purpose of refrigeration cycle is, removal of heat from the lower temperature and rejecting it at the temperature of surroundings, i.e.:

$$COP_{\text{refrig}} = \frac{refrigerating \ effect}{work \ input}$$
(2)

In case of heat pumps the desired effect is heating of a space, i.e. heat is rejected to the higher temperature, and then:

$$COP_{\text{heat pump}} = \frac{heating \ effect}{work \ input}$$
(3)

The most common types of refrigeration systems use the vapor compression refrigeration cycle although absorption heat pumps are used in some applications, gaining wider acceptance in the light of the fact that so called trigeneration is perceived as a way to introduce more efficient use of heat in summer in back-pressure heat and power plants.

Cyclic refrigeration can be classified as:

- Vapor cycle,
- Vapor compression refrigeration
- Gas absorption refrigeration
- Gas cycle

Heat naturally flows from hot to cold. Work must be applied to cool a living space or storage volume by pumping heat from a lower temperature heat source into a higher temperature heat sink. Insulation is used to reduce the work and energy required to achieve and maintain a lower temperature in the cooled space. The operating principle of the refrigeration cycle was described mathematically by Sadi Carnot in 1824 on the example of reversible heat engine. That analysis is also applicable to refrigeration cycles, provided a reverse sequence of processes is considered.

2.2.1. Carnot Cycle

The Carnot cycle is a theoretical model that is useful for understanding the principles of operation of a refrigeration cycle. The Carnot cycle is an ideal model for the heat engine, however, being the ideal cycle, it can be considered in refrigeration also when the processes are executed in the anti-clockwise manner. The maximum theoretical performance can then be calculated, establishing criteria against which real refrigeration cycle, as shown in Figure 2 and Figure 3:

- Ideal compression at constant entropy. During the process temperature of refrigerant increases and work is required to be input (process 1-2).
- Rejection of heat in the condenser at a constant condensation temperature, $T_{\rm H}$ (process 2-3).
- Ideal expansion at constant entropy. During the process temperature of the refrigerant decreases, (process 3-4)
- Absorption of heat in the evaporator at a constant evaporation temperature, $T_{\rm L}$ (process 4-1)



Figure 2. Basic elements of Carnot refrigeration cycle.

The efficiency of the Carnot refrigeration cycle is determined with the aid of coefficient of performance (COP) which expresses the ratio of the heat required for evaporation of working fluid, Q_0 to the expense of the cycle, in our case work required to drive the cycle, W:

$$COP = \frac{\dot{Q}_o}{W}$$

(4)



Figure 3. T - s diagram of the Carnot refrigeration cycle.

In the case of Carnot refrigeration cycle the particular components of relation (4) can be determined in terms of temperatures of higher and lower heat sources and corresponding entropies. Then we obtain the coefficient of performance in terms of higher and lower temperatures of heat sources in the form:

$$COP = \frac{T_{\rm L}}{T_{\rm H} - T_{\rm L}} \tag{5}$$

Examination of relation (5) tells us that in case when lowest possible work is demanded then $T_{\rm H}$ should be as low as possible whereas $T_{\rm L}$ should be as high as possible for refrigeration applications.

Perfect isothermal processes cannot be obtained with gases as working fluids since such processes require either infinitely low rates of expansion or compression to maintain the temperature rigorously constant at a finite heat transfer rate or infinitely high rates of heat transfer at finite rates of expansion or compression.

2.2.2. Lorenz Cycle

Due to the fact that more and more often are found variable saturation temperatures in evaporators and condensers which disable application of the Carnot ideal cycle and to facilitate appropriate analysis the Lorenz cycle is usually incorporated. Such situation is

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present during the isobaric phase change of zeotropic mixtures where changes of saturation temperature are a result of the change of mixture composition. The sequence of executed processes is presented in Fig. 4. Formally, this cycle can be regarded as a refrigeration Joule cycle, which is a gas cycle, but processes employed are within the vapor region. Sometimes the Lorenz cycle is regarded as a Carnot cycle with variable temperatures. Coefficient of performance is defined as:

$$COP = \frac{T_{\mathrm{L}_{\mathrm{M}}}}{T_{\mathrm{H}_{\mathrm{M}}} - T_{\mathrm{L}_{\mathrm{M}}}} \tag{6}$$

The representative temperatures present in relation (6) can be found from the expressions:

$$T_{\rm L_M} = \frac{1}{s_1 - s_4} \int_{s_4}^{s_1} T_{\rm L} ds \qquad T_{\rm L_M} = \frac{1}{s_2 - s_3} \int_{s_3}^{s_2} T_{\rm H} ds \tag{7}$$

Sometimes it is practical to use simplified expressions with arbitrarily assumed logarithmic means of saturation temperatures:



Figure 4: The Lorenz cycle.

The above values of temperatures result from the conditions of heat transfer in evaporator and condenser. Logarithmic distributions of temperature are obtained in case of homogeneous heat transfer conditions in these heat exchangers.

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Biographical Sketches

Dariusz Mikielewicz, born in 1967. He received his Master of Science degree from the Gdansk University of Technology in the area of Refrigeration Technology in 1990. Subsequently he completed his doctoral education at the Victoria University of Manchester, Great Britain, where he was awarded a PhD degree from the Mechanical and Nuclear Engineering Department in 1994 for the studies on the performance of turbulence models in modeling of mixed convection in tubes. He then joined in 1994 the Nuclear Electric plc, where he was an engineer involved with the development of the safety reactor code Panther. In 1996 he returned to Poland, where he took up employment at the Faculty of Mechanical Engineering of Gdansk University of Technology (FME GUT) at the Heat Technology Department, and where he is still employed. In 2002 he was awarded the Doctor of Science degree (habilitation) by the Board of FME GUT for the studies into modeling of two-phase flows in boundary layers. From 2004 he is employed as a professor at FMW GUT. Since 2004 he is an elected member of the Council for Science at the Ministry for Science and Higher Education. His research interests include modeling of single and two-phase heat transfer in conventional and small diameter channels, jets and sprays, microjets, and renewable energy.

Jarosław Mikielewicz, born in Vilnus, Poland, 10 April 1941. **Education**: received all the academic titles from the Gdansk University of Technology, Poland, namely the MSc in Mechanical Engineering in 1964, Ph.D. (Mechanical Engineering) in 1968 and Doctor of Science (habilitation) in 1972. The title of Professor was awarded to him in 1979 by the President of State Council of Poland. He received the honorary Doctor of Engineering degree from the Technical University of Cracow in 2004. He has been elected a Corresponding Member to the Polish Academy of Sciences in 2002. Currently he is the President of Editorial Board of the international journal Archives of Thermodynamics and the President

CHEMICAL ENGINEERING AND CHEMICAL PROCESS TECHNOLOGY – Vol. II - Refrigeration - D. Mikielewicz, J. Mikielewicz

of Editorial Board of the Transactions of the Institute of Fluid Flow Machinery PASci. He served as faculty member at several universities and scientific boards of scientific institutions etc. **Current Position**: Full Professor, Head of the Institute of Fluid Flow Machinery Polish Academy of Sciences, Gdansk and Professor at the Technical University Koszalin, Poland. **Fellowships:** Institute of Thermal Technology of Russian Academy of Sciences, Novosibirsk 1970, American Academy of Sciences in: MIT Heat Transfer Laboratory, University of Delaware, University of Michigan, 1974, Visiting Full Professor, Brown University, Providence RI, USA 1981/1982, German Academy of Sciences (DAAD) in various German Universities 1986. American Academy of Sciences in various American Universities (Rennselear Polytechnic Institute) 1988. fellowship in McMaster University, Canada 1992. Author or co-author of above 170 papers. **Research Interests**: include nuclear plant safety analysis, heat transfer (flow boiling), fluid mechanics (two-phase flow, thin liquid films), thermodynamics, renewable energy in variety of application areas.

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