LA-11102-MS

UC-66b

Issued: March 1988

LA--11102-MS

DE88 007080

*Active Cooling for Downhole Instrumentation:
Preliminary Analysis and System Selection*

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MASTER

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ACTIVE COOLING FOR DOWNHOLE INSTRUMENTATION:
PRELIMINARY ANALYSIS AND SYSTEM SELECTION

by

Gloria A. Bennett

ABSTRACT

A feasibility study and a series of preliminary designs and analyses were done to identify candidate processes or cycles for use in active cooling systems for downhole electronic instruments. A matrix of energy types and their possible combinations was developed and the energy conversion process for each pair was identified. The feasibility study revealed conventional as well as unconventional processes and possible refrigerants and identified parameters needing further clarification.

A conceptual design or a series of designs for each system was formulated and a preliminary analysis of each design was completed. The resulting coefficient of performance for each system was compared with the Carnot COP and all systems were ranked by decreasing COP. The system showing the best combination of COP, exchangeability to other operating conditions, failure mode, and system serviceability is chosen for use as a downhole refrigerator.

I. INTRODUCTION

This report describes a feasibility study and a series of conceptual designs and analyses done to identify and sort candidate processes for use in an active cooling system for downhole electronic instruments. The detailed design criteria and an extensive description of the environment and conditions encountered in hot geothermal wellbores are given in an earlier report.¹

The objective of this work is to provide a rational basis from which to select a refrigeration process for extensive engineering design and analysis.

The objective of the feasibility study was to identify both conventional and unconventional processes for refrigeration. This study also provided a first-level sorting of the many possible energy combinations that hold promise for further investigation.

The objective of this system design is to move a given quantity of heat from a cold reservoir to a hot reservoir. The maximum heat load is assumed to be 8 W and the cold reservoir is assumed to be the entire electronic instrument compartment that must be maintained at or below 150°C. The hot reservoir is assumed to be a hot geothermal wellbore at or below 320°C. A refrigeration system might be subjected to the following conditions:

Temperature	-- $0^{\circ}\text{C} < T < 320^{\circ}\text{C}$
Pressure	-- $0 \text{ Pa} < P < 82.7\text{E}+06 \text{ Pa}$
pH	-- $2 < \text{pH} < 12$
Suspended solids	-- 10,000 ppm
Vibration	-- $10 \text{ Hz} < 400$
Impact	-- up to 15 g's.

The design criteria and relevant constraints are summarized as follows:

Refrigeration load	-- 8 W
Power input	-- 22 W
COP minimum	-- 0.363
Hot reservoir	-- 320°C
Cold reservoir	-- 150°C
Power	-- 110 Vac @ 200 mA
Shape	-- right circular cylinder
Size	-- 6-in. o.d. x approximately 2-ft long
Weight	-- 50 lb.

II. FEASIBILITY STUDY

The first step in a feasibility study involves a systematic search for possible solutions to the problem. The central purpose of this search is to discover unconventional processes that might not otherwise be considered under the constraints imposed on this particular system design. Because a refrigeration process involves heat transfer, it is reasonable to expect that heat energy must be involved in any candidate process. Other forms of energy that can be coupled with heat and converted in some process are included in the search.

Table I is a matrix of energy types that might be coupled with both heat and electricity. The specific energy conversion cycle or energy "effect" relating a pair of energy types is identified. Not all entries in this table will result in an engine or a refrigerator. Table II is an expanded list of each entry that gives the specific process name, the process, and a common refrigerant. The following processes or energy "effects" were identified as starting candidates: Rankine cycle, Brayton cycle, absorption refrigeration, Joule-Thompson cooling, thermoelectric cooling, magnetocaloric refrigeration, electrocaloric refrigeration, the surface heat pumping cycle, and fuel cells. The following paragraphs describe results of a cursory search into each topic.

Rankine cycles that use water as the heat transfer medium are the most common in industry. Limits on the practical use involve high pressures for temperatures near the critical point. Many other refrigerants are available for low-temperature uses, and several organic fluids might be used at high temperatures in this application.^{2,3}

Brayton cycles are the only gas cycles commonly used for refrigeration purposes, namely in aircraft applications. The major drawbacks involve the much larger flow rates of air, as opposed to fluid, for the same heat removal.⁴ Other gases worth investigating as refrigerants include helium and hydrogen.

Joule-Thompson cooling has been done primarily at cryogenic temperatures -193 to -173°C to cool electronic sensors and hardware that are space or flight qualifiable.⁵ The refrigerant generally used is nitrogen, but other gases could be investigated to determine their inversion temperatures.

TABLE I
MATRIX OF CANDIDATE ENERGY TYPES

<u>Energy Type</u>	<u>Heat</u>	<u>Electricity</u>
Mechanical	Vapor compression; gas cycles	Flywheels
Heat	-----	Electrocaloric capacitors; Thermoelectric semiconductors
Electrical	Electrocaloric capacitors; thermoelectrics	-----
Magnetic	Magnetocaloric effect	Electromagnetic fields
Chemical	Absorption refrigerators	Fuel cells
Acoustic	Surface heat pumping; Taconis oscillations	-----
Atomic	Fission; fusion	+,-Charged particle beams
Light	Solar radiation	Photoelectric effect
Wind	Natural convection	Windmills
Hydraulic	Geothermal	Hydrothermal

TABLE II
MATRIX OF CANDIDATE REFRIGERATION PROCESSES

<u>Description</u>	<u>Energy Types</u>	<u>Process</u>	<u>Common Refrigerants</u>
Rankine Cycle	Heat-mechanical	Phase change, gas expansion	Water, Freon
Brayton Cycle	Heat-mechanical	Isentropic gas expansion	Air
Joule-Thompson	Heat-mechanical	Isenthalpic gas expansion	Nitrogen
Surface heat pumping	Heat-acoustic	Polytropic gas expansion	Helium
Absorbtion refrigerator	Heat-chemical	Concentration Δ change	Ammonia-water, Lithium-Bromide- Water
Thermoelectric	Heat-electrical	Peltier effect	Bismuth-Tellurium and Antimony-Tellurium
Magnetocaloric	Heat-magnetic	Magnetic field Δ at Curie Point	Gadolinium
Electrocaloric	Heat-polarization	Permittivity Δ at Curie Point	Barium Titanate
Fuel cells	Electro-chemical	Ion and charge Δ	Hydrogen-oxygen

The energy available from acoustic vibrations has been investigated for use as an engine, and more recently, for use in heat pump and refrigeration applications at cryogenic temperatures.⁶ The surface heat pumping cycle is a modified gas cycle on a microscopic scale that would probably use the same refrigerant gases.

The absorption refrigeration process is also common in industry and is used in applications that have access to moderate temperature waste heat. This system design might lend itself to using the wellbore heat as the heat source to drive the part of the cycle that is the heat equivalent of the compressor. Common refrigerants are ammonia-water and lithium-bromide, which are used in ambient air conditioning systems. These systems, however, are bulkier than vapor compression systems and generally require more maintenance.⁷

Thermoelectric refrigeration is done for heat loads with small temperature differences. The common applications include cooling in systems that are physically small or are not suitable for pumped fluid applications. The common semiconductor pairs used at about room temperature are bismuth-tellurium and antimony-tellurium.⁸ Other semiconductor pairs have been developed that function at very high temperatures, but the major drawback for any thermoelectric system is the very low efficiency of the device (3-10%).⁹

The electrocaloric and magnetocaloric systems have been studied for use as direct energy converters.⁹ The electrocaloric system has been used as an engine with barium titanate as the dielectric refrigerant material in the capacitor. The magnetocaloric system has been used to produce refrigeration at cryogenic temperatures at Los Alamos.¹⁰ Both systems are in the research stages; only the transition metals that exhibit ferromagnetism and have medium temperature Curie points would be suitable as refrigerants.

The direct conversion of chemical energy to electrical energy is accomplished using a fuel cell. Research has been done on fuel cell applications for engine replacements and for cogeneration of electric power, but a cycle using a fuel cell would have to work in reverse to be applicable for use as a refrigerator.¹¹

III. PRELIMINARY DESIGNS AND ANALYSES

A preliminary design or a series of designs for each candidate system was made and analyzed. Each analysis included all the relevant engineering parameters in an ideal, or a simplified, formulation. Each analysis resulted in a coefficient of performance (COP) that is the ratio of heat extracted from the cold reservoir to the energy input necessary for the functioning of the refrigerator. The COP for each system was used to rank it in decreasing order of feasibility when compared with the Carnot COP.

The following chapters contain a brief background of each refrigeration process and an outline of the theory and its application to an engine and to a refrigerator suitable for use in this work. Each analysis for which there is a suitable refrigerant results in a set of specifications that define component sizes and the operation or the predicted performance of the process.

IV. VAPOR COMPRESSION REFRIGERATION

A. Single-Stage Vapor Compression System

Refrigeration can be accomplished using a vapor compression power cycle operated in reverse.¹² The major components are shown schematically in Fig. 1 and include a gas compressor, a high-pressure condenser heat exchanger, an expansion valve, and a low-pressure evaporator heat exchanger. Figure 2 illustrates an ideal Carnot refrigeration cycle that operates entirely under the refrigerant vapor dome. This cycle is not practical because the compression must be carried out on a wet vapor mixture. To avoid this difficulty in practice, cycles are run using the temperature-entropy diagram shown in Fig. 3. The compression process in this cycle is done on a gas.

B. Theory

The Rankine refrigeration cycle shown in Fig. 3 most resembles the Carnot cycle and it is the simplest cycle in practical use. The thermodynamic state of a refrigerant is defined by three of its thermodynamic properties, a process is defined by its end states, and a cycle is a combination of processes that describe a closed curve on a property diagram. The Rankine refrigeration cycle involves two isobaric processes: an isenthalpic process and an isentropic process.

Fig. 1. Schematic of vapor-compression refrigerator.

Fig. 2. Carnot cycle temperature-entropy diagram.

Fig. 3. T-S diagram for vapor-compression refrigerator.

The working fluid, or refrigerant, absorbs heat in the evaporator, causing the wet vapor to be completely evaporated at constant temperature and pressure from State 1 to State 2. The heat absorbed per unit mass of refrigerant is given by

$$q_{1-2} = h_2 - h_1 \quad . \quad (1)$$

The fluid at State 2 is in the saturated vapor state at low temperature and pressure when it enters the suction side of the compressor. The compression process raises the vapor temperature and pressure to a superheated vapor condition at State 3. The compression process is fast enough to be considered adiabatic and as close to isentropic as possible. The ideal "heat of compression" or the work input to the compressor per unit mass of refrigerant is given by

$$W_{2-3} = h_3 - h_2 \quad . \quad (2)$$

This quantity is increased because of friction, pressure drop at the valves, heat transfer to the surroundings, and the extra gas left in the cylinder after each stroke. The actual work input to the compressor is given by

$$W_{act} = \frac{W_{2-3}}{\eta} \quad , \quad (3)$$

where η is the compressor efficiency. Heat is rejected from the superheated vapor at State 3 at constant pressure, changing it to a saturated vapor state in the condenser where it undergoes further cooling at constant temperature and pressure until it reaches a condensed saturated liquid state at Point 4. The heat rejected from the condenser per unit mass of refrigerant is given by

$$q_{4-3} = h_3 - h_4 \quad . \quad (4)$$

The saturated vapor at high temperature and pressure then undergoes a constant enthalpy expansion back to a low-pressure, low-temperature wet vapor mixture at State 1. The expansion valve also serves to regulate the flow of refrigerant to keep the condenser full of liquid and to allow only as much refrigerant into the evaporator as can be completely vaporized.

Refrigerant in the system undergoes continuous changes in state from Points 1-2-3-4-1. The efficiency of the refrigeration cycle is given by the coefficient of performance as

$$\text{COP} = (h_2 - h_1) / (h_3 - h_2) \quad .^{12} \quad (5)$$

The capacity for refrigeration is determined by the quantity of refrigerant flowing in the cycle. The total heat absorbed in the evaporator is then

$$\dot{Q}_{\text{abs}} = \dot{m} q_{1-2} \quad . \quad (6)$$

From an energy balance on the system, the quantity of heat rejected by the condenser must be equal to the heat absorbed in the evaporator plus the actual heat of compression added to the system. The total heat rejected is then

$$\dot{Q}_{\text{reject}} = \dot{Q}_{1-2} + \dot{W}_{\text{act}} \quad . \quad (7)$$

C. Component Sizing

The size or capacity of each component can be determined after the flow rate is known. The system plumbing can be specified, using the condenser temperature and pressure and the pressurized piping standards. The minimum tubing thickness is given by

$$t_m = \frac{PD}{2S + yP} + C \quad ,^{13} \quad (8)$$

where P = maximum internal service pressure,
 D = piping outside diameter,
 S = allowable stress,
 y = coefficient,
 C = allowance for threading and corrosion, and
 t_m = minimum pipe wall thickness.

The heat exchangers are sized assuming a simple arrangement with the refrigerant flowing inside the tubing and a coolant flowing or stagnant on the outside. The required heat transfer area in both the evaporator and the condenser can be determined using the equation

$$Q = UA\Delta T_{LM} \quad ,^{14} \quad (9)$$

where Q = heat transferred,
 U = overall heat transfer coefficient,
 A = heat transfer area, and
 ΔT_{LM} = log mean temperature difference.

The overall heat transfer coefficient is determined by summing the individual resistances to heat flow and is given by

$$\frac{1}{U} = \frac{1}{f_o} + \frac{A_o}{A_i} \cdot \frac{1}{f_i} + \frac{A_o}{A_m} \cdot \frac{X}{K} \quad ,^{15} \quad (10)$$

where U = overall heat transfer coefficient,
 f_o = outside film coefficient,
 f_i = inside film coefficient,
 A_o = outside area,
 A_i = inside area,
 A_m = mean tubing area,
 X = tubing thickness, and
 K = tubing conductivity.

The approach temperatures commonly used in current refrigeration designs of condensers and evaporators are approximately 7-14°C. Solving for area gives the minimum required heat transfer area as

$$A_{min} = \frac{Q}{U \Delta T_{LM}} \quad (11)$$

Pressure drops through the system can be estimated once the tubing diameters and the heat exchanger sizes are known. Then, applying the equation for friction head loss we get

$$\Delta p = F_{d-w} \cdot \frac{L}{D} \cdot \rho \cdot \frac{v^2}{2g_c} \quad (12)$$

where F_{d-w} = Darcy-Weisbach friction factor,

L/D = dimensionless length,

ρ = fluid density,

v = fluid velocity, and

g_c = gravitational constant.

The available pressure drop across the expansion valve is then given by

$$\Delta p_{4-1} = P_4 - (P_1 + P_a + P_v) \quad (13)$$

where P_4 = lowest condenser pressure,

P_1 = highest evaporator pressure,

P_a = pressure drop across accessories between Hx's, and

P_v = pressure drop from refrigerant vertical lift.

The pressure increase required from the compressor is

$$\Delta P_{3-2} = P_3 - P_2 \quad (14)$$

where P_3 = highest condenser pressure, and

P_2 = lowest evaporator pressure.

The compressor capacity or piston displacement must be large enough to compress the vapor being produced by the evaporator without causing pressure increases above State 1. The actual piston displacement is given by

$$PD = \dot{M}V_1 / N\eta \quad ,^{12} \quad (15)$$

where η = compressor efficiency,

PD = piston displacement,

$\dot{M}$ = fluid mass flow rate,

N = rotation rate of the compressor, and

V_1 = specific volume of fluid at State 1.

The compressor must have the above displacement capacity between the lowest and highest pressures at a given flow rate. The heat exchangers must have the minimum areas as determined above, and the expansion valve must be capable of producing the stated pressure drop at the stated flow rate.

D. Preliminary Analysis

1. Single-Stage Refrigerators. A preliminary analysis was made using water as a refrigerant and assuming that the heat exchange processes provide only saturated vapor in the evaporator and saturated liquid in the condenser. This cycle would require a receiver to store liquid refrigerant below the condenser and a thermostatically controlled or a pressure regulating throttling valve. Only a compressor, heat exchangers, and a throttling valve are considered.

The refrigerant undergoes a cycle as shown in Fig. 3, with the properties at each state point given in Table III.¹⁷ The results of the calculations are shown in Table IV for both the ideal and nonideal quantities. Each component of the cycle was sized and is specified using the stated assumptions and parameters as listed in Table V.

The results show that an ideal vapor compression refrigeration cycle using steam has 44% of the Carnot COP. This cycle is feasible, even though it is relatively unattractive because of the high temperatures and pressures required in the condenser.

TABLE III
REFRIGERANT PROPERTIES -- STEAM^a

<u>Point</u>	<u>State</u>	<u>T(°F)</u>	<u>P(psia)</u>	<u>h(Btu/lb)</u>	<u>s(Btu/lb-R)</u>
1	Wet vapor	300	67.01	616.8	0.894
2	Sat. vapor	300	67.01	1179.7	1.635
3	Super. vapor	1100	1543.2	1548.3	1.635
4	Sat. liquid	600	1543.2	616.8	0.813

^a Ref. 17.

TABLE IV
SINGLE-STATE VAPOR COMPRESSION REFRIGERATOR
RESULTS: IDEAL AND NONIDEAL QUANTITIES

	<u>Ideal</u>	<u>Nonideal</u>
Q _{absorb}	27.3 Btu/h	27.3 Btu/h
Power Input	17.8 Btu/h	25.1 Btu/h
Flow Rate	0.0485 lb/h	0.0485 lb/h
COP	1.527	1.087

TABLE V
SINGLE-STAGE VAPOR COMPRESSION REFRIGERATOR
PRELIMINARY COMPONENT SPECIFICATIONS

Compressor	p = 1475 psia @ $\dot{m}$ = 0.0485 lb/h η = 0.71, P_H/P_L = 23, CF = 0.03
Expansion Valve	p = 1475 psia @ 0.0485 lb/h
Condenser	Q _{reject} = 52.4 Btu/h, ΔT = 18°F U = 45 Btu/h ft ² -°F, A _{min} = 9.5 in. ²
Evaporator	Q _{absorb} = 27.3 Btu/h, ΔT = 18°F U = 41 Btu/h ft ² -°F, A _{min} = 45 in. ²
Tubing ^a	t _m = 0.079 in. Schedule 80 1/8-in. o.d. ASTM A312 with welded connections σ_{allow} = 10,300 psi T = 1100°F Stainless steel

^aRef. 21.

A similar preliminary analysis of a single-stage vapor compression refrigerator using thermex (Dowtherm A) refrigerant was made.¹⁸ The refrigerant components are arranged, as shown in Fig. 1, and the refrigerant moves through the thermodynamic cycle (Fig. 4). This cycle is not a conventional Rankine refrigeration cycle because the heat exchanger absorbing heat at the cold reservoir temperature operates entirely on gas and does not function as an evaporator. Table VI lists the state points in the cycle, using the appropriate temperatures for the heat source and heat sink. The isenthalpic process that starts at Point 4 on the saturated liquid line reaches the saturated vapor line at a temperature higher than the required heat source temperature, which is labeled as State Point 1. For this reason, thermex cannot function as a refrigerant for a vapor compression cycle between the temperatures required for this application.

A preliminary study of the properties of mercury¹⁹ shows that it is not suitable as a refrigerant for this application for the following reasons: (a) the vapor pressure at 150°C is below atmospheric pressure and would require a vacuum on the evaporator side of the system; (b) air leaks into the evaporator side of the system would create considerable problems with pressure balance; (c) corrosion with the mercury changing phase is serious and gets worse in the presence of oxygen or air leaks into the system piping; and (d) mercury is very toxic in vapor form.

For these reasons, neither thermex nor mercury are considered feasible for use as a single-stage vapor compression refrigerant.

2. Single-Stage Refrigerator with Preheater. An analysis of a vapor compression refrigerator with a preheater was made using water as a refrigerant.²⁰ The additional heat exchanger provides a slight amount of superheat to the vapor leaving the evaporator and an equivalent amount of subcooling for the liquid leaving the condenser.

The additional countercurrent heat exchanger used as a preheater is arranged as shown in Fig. 5. The refrigerant moves through a cycle (Fig. 6). The properties for each state point are shown in Table VII. The results of the calculations are shown in Table VIII for both an ideal and a nonideal cycle. Each component was sized according to previous sections stating design criteria as listed in Table IX.²¹

Fig. 4. T-S diagram for thermex refrigerator.

Fig. 5. Vapor-compression refrigerator with preheater.

Fig. 6. T-S diagram for refrigerator with preheater.

TABLE VI
REFRIGERANT PROPERTIES -- THERMEX^a

<u>Point</u>	<u>State</u>	<u>T(°F)</u>	<u>P(psia)</u>	<u>h(Btu/lb)</u>	<u>s(Btu/lb-R)</u>
1	Sat. vapor	318	0.94	255.1	≈0.75
1 ¹	Sat. vapor	300	0.63	248.2	0.75
2	Super. vapor	~455	~1.0	310	0.83
3	Sat. vapor	600	45.5	371.3	0.83
4	Sat. liquid	600	45.5	255.1	0.724

^aRef. 18.

TABLE VII
VAPOR COMPRESSION REFRIGERATOR WITH PREHEATER
REFRIGERANT PROPERTIES -- STEAM^a

<u>Point</u>	<u>State</u>	<u>T(°F)</u>	<u>P(psia)</u>	<u>h(Btu/lb)</u>	<u>s(Btu/lb-R)</u>
1	Wet vapor ^b	300	67.01	588.9	0.8573
2	Sat. vapor	300	67.01	1179.7	1.635
2'	Super. vapor	351	67.01	1207.6	1.6704
3	Super. vapor	1296	1543.2	1661.3	~1.6704
4	Sat. liquid	600	1543.2	616.8	0.813
4	Sub. liquid	580	~1543.2	588.9	~0.7872

^aRef. 17.

$$^b \quad x = \frac{h_1 - h_f}{\Delta h_{fg}} = \frac{588.9 - 269.59}{910.1} = 0.3509,$$

is the quality of the wet vapor at point 1.

TABLE VIII

VAPOR COMPRESSION REFRIGERATOR WITH PREHEATER
RESULTS: IDEAL AND NONIDEAL QUANTITIES

	<u>Ideal</u>	<u>Nonideal</u>
Q_{absorb}	27.3 Btu/h	27.3 Btu/h
Power_{in}	20.96 Btu/h	29.48 Btu/h
Flow Rate	0.0462 lb/h	0.0462 lb/h
COP	1.302	0.926
Comparison with Rankine refrigeration	85%	85%

TABLE IX

VAPOR COMPRESSION REFRIGERATOR WITH PREHEATER
PRELIMINARY COMPONENT SPECIFICATIONS

Compressor	$p = 1475 \text{ psi}$ @ $\dot{m} = 0.0485 \text{ lb/h}$ $\eta = 0.71$, $P_H/P_L = 23$, $CF = 0.03$
Expansion Valve	$p = 1475 \text{ psia}$ @ 0.0485 lb/h
Condenser	$Q_{\text{reject}} = 56.8 \text{ Btu/h}$, $\Delta T = 18^\circ\text{F}$ $U = 45 \text{ Btu/h ft}^2\text{-}^\circ\text{F}$, $A_{\text{min}} = 10.1 \text{ in.}^2$
Evaporator	$Q_{\text{absorb}} = 27.3 \text{ Btu/h}$, $\Delta T = 18^\circ\text{F}$ $U = 41 \text{ Btu/h ft}^2\text{-}^\circ\text{F}$, $A_{\text{min}} = 45 \text{ in.}^2$
Tubing ^a	$t_m = 0.079 \text{ in.}$ Schedule 80 1/8-in.o.d. ASTM A312 with welded connections $\sigma_{\text{allow}} = 10,300 \text{ psi}$ $T = 1100^\circ\text{F}$ Stainless steel

^aRef. 21.

The results show that the additional heat exchanger decreases the required flow rate by 5% and decreases the COP by 15%. The condenser requires a slightly larger heat transfer area by about 6%, with only a very small area required for the preheater.

The COP for this cycle is 37% of the Carnot COP, making this system feasible but still unattractive because of the large compression ratio required of the compressor.

3. Two-State Vapor Compression Refrigerator. An analysis was made of a two-stage vapor compression refrigerator using water as the first-stage and thermex as the second-stage refrigerant. The calculations for a two-stage cycle were done to minimize the compression ratio required by a single-stage system design.²⁰

Steam moves through the cycle at State Points 1-2-3-4 (Fig. 7) and the thermex moves through State Points 1A-2A-3A-4A. The thermodynamic properties of both fluids are listed in Table X. A schematic of the system components is shown in Fig. 8 and requires an evaporator, two compressors, an intermediate heat exchanger, a condenser, and two throttling valves. The results of the calculations are given in Table XI for an ideal and a nonideal cycle. Each component size was determined according to previously stated design criteria and is listed in Table XII.

The results show that the addition of a second stage reduces the compression ratio from 23 to 7 for both stages, which is considerably more practical. Even though this system requires an additional compressor, heat exchanger, and expansion valve, the COP is higher than the COP for either the single-stage cycle or for the single-stage cycle with a preheater. The flow rate required in the second stage is about 10 times larger than that required for the first stage, and, therefore, requires a larger intermediate heat exchanger and condenser.

This system is feasible for use in this cooling application.

E. Summary. Preliminary scoping calculations have been made for various vapor compression refrigeration cycles and refrigerants. A single-stage system using water as the refrigerant is feasible, but unattractive, because the compression ratio of 23 is too large to be practical. Calculations for a single-stage cycle with a preheater yield a

Fig. 7. T-S diagram for two-stage vapor-compression refrigerator.

Fig. 8. Two-stage vapor-compression refrigerator.

TABLE X
REFRIGERANT PROPERTIES -- STEAM AND THERMAX

Point	State	T(°F)	P(psia)	h(Btu/lb)	s(Btu/lb-R)
1	Wet vapor ¹	300	67.01	441.4	0.663
2	Sat. vapor	300	67.01	1179.7	1.635
3	Super. vapor	730	466.9	1375	1.635
4	Sat. liquid	460	466.9	441.4	0.6402
1A	Wet vapor ²	440	7.18	255.1	-----
2A	Super. vapor	550	7.18	350	0.829
3A	Sat. vapor	600	45.55	371.3	0.829
4A	Sat. liquid	600	45.55	255.1	0.724

Wet vapor quality:

$$1 \quad x_1 = \frac{h_1 - h_f}{h_2 - h_f} = \frac{441.4 - 269.59}{1179.7 - 269.59} = 0.189,$$

$$2 \quad x_{1A} = \frac{h_{1A} - h_{fA}}{h_{2A} - h_{fA}} = \frac{255.1 - 169.6}{133.6} = 0.64.$$

TABLE XI
TWO-STAGE VAPOR COMPRESSION REFRIGERATOR
RESULTS: IDEAL AND NONIDEAL QUANTITIES

	<u>Ideal</u>	<u>Nonideal</u>
Q _{absorb}	27.3 Btu/h	27.3 Btu/h
Q _{reject}	42.24 Btu/h	48.3 Btu/h
Power _{in}	14.96 Btu/h	21.04 Btu/h
Flow Rate	$\dot{m}_I = 0.0369 \text{ lb/h}$ $\dot{m}_{II} = 0.3635 \text{ lb/h}$	
COP	1.82	1.29

TABLE XII

TWO-STAGE VAPOR COMPRESSION REFRIGERATOR
PRELIMINARY COMPONENT SPECIFICATIONS

Compressor _I	$P_I = 400 \text{ psi}, r = \frac{P_H}{P_L} = 7$ for $\eta = 0.711$, $CF = 0.03$ $\dot{m} = 0.0369 \text{ lb/h steam}$
Compressor _{II}	$P_{II} = 39 \text{ psi}, r = 6.3$ $\eta = 0.711$, $CF = 0.03$ $\dot{m} = 0.3635 \text{ lb/h Thermex}$
Expansion Valve _I	$P_I = 400 \text{ psi @ } 0.0369 \text{ lb/h Steam}$ $P_{II} = 38 \text{ psi @ } 0.3635 \text{ lb/h Thermex}$
Evaporator	$Q_{\text{absorb}} = 27.3 \text{ Btu/h}, \Delta T = 18^\circ\text{F}$ $U = 4.8 \text{ Btu/h-ft}^2\text{-}^\circ\text{F},$ $A_{\text{min}} = 46 \text{ in.}^2$
Heat Exchanger	$Q_{\text{transfer}} = 37.5 \text{ Btu/h}, \Delta T = 20^\circ\text{F}$ $U = 40.2 \text{ Btu/h-ft}^2\text{-}^\circ\text{F},$ $A_{\text{min}} = 7 \text{ in.}^2$
Condenser	$Q_{\text{reject}} = 48.3 \text{ Btu/h}, \Delta T = 18^\circ\text{F}$ $U = 39.5 \text{ Btu/h-ft}^2\text{-}^\circ\text{F},$ $A_{\text{min}} = 8 \text{ in.}^2$
Tubing ^a	$t_m = 0.057 \text{ in.}$ Schedule 40 1/8-in. o.d. $\sigma_{\text{allow}} = 14,800 \text{ psi}$ $T = 750^\circ\text{F}$ Stainless steel

^aRef. 21.

smaller flow rate and a decreased COP, but a larger required heat transfer area. This system is feasible but also unattractive because of the large compression ratio and additional piping for the added heat exchanger. A calculation of a single-stage cycle using thermex as the refrigerant results in a cycle that is not a conventional vapor compression system, because the source heat exchanger operates only on superheated vapor and does not operate as an evaporator. A preliminary examination of the properties of mercury show that it would require a vacuum-tight piping system and would be extremely susceptible to corrosion. For these reasons, thermex and mercury are not considered as candidate refrigerants.

The calculations of a two-stage cycle using water in the first stage and thermex in the second stage produce a feasible system with compression ratios of about 7 in each stage. The two-stage system is determined to be the only viable choice of vapor compression refrigeration for this application.

V. BRAYTON REFRIGERATION CYCLE

A. System

Refrigeration can be accomplished using the Brayton power cycle in reverse. The major components are shown schematically in Fig. 9 and include a gas compressor, a high-temperature heat exchanger, an expander, and a low-temperature heat exchanger. The most practical circumstance for using an air cycle refrigerator occurs if power for compression is available from another source and can be used to decrease the total work input. Compared with the Rankine cycle, the Brayton cycle is less efficient because the heat transfer occurs during constant pressure processes rather than occurring isothermally. In addition, this cycle requires comparatively large amounts of gas to be compressed and expanded to produce an equivalent cooling effect. The Brayton cycle is the only gas cycle used for commercial refrigeration purposes.²²

B. Theory

The ideal Brayton refrigeration cycle (Fig. 10) consists of two constant pressure processes: an isentropic compression and an isentropic expansion. The assumptions used in the preliminary analysis are the following:

Fig. 9. Brayton refrigeration cycle schematic.

Fig. 10. Temperature-entropy diagram for Brayton refrigeration cycle.

- a) the processes are reversible,
- b) the specific heats are constant, and
- c) the gas refrigerant behaves as a perfect gas.

This four-component Brayton cycle is the simplest gas cycle used for refrigeration. The working fluid, or gas refrigerant, absorbs heat in the low-temperature heat exchanger during a constant pressure process at P_{10} , causing the temperature to increase. The "cooling effect" or the heat absorbed per unit mass of refrigerant is given by

$$q_{1-2} = h_2 - h_1 = C_p (T_2 - T_1) \quad . \quad (16)$$

The gas temperature at State 2, as it enters the suction side of the compressor, is slightly below the cooling load temperature. Compression raises the refrigerant temperature and pressure to their highest values in the cycle. The process is fast enough to be adiabatic and is considered isentropic. The temperature at the end of the compression process is given by

$$T_{hi} = T_{lo} \times \left(\frac{P_{hi}}{P_{lo}} \right)^{\frac{\gamma-1}{\gamma}} \quad . \quad (17)$$

The ideal "heat of compression" or work input per unit mass of the refrigerant is:

$$W_{2-3} = h_3 - h_2 = C_p (T_3 - T_2) \quad . \quad (18)$$

The gas is then cooled at constant pressure, P_{hi} , in the high-temperature heat exchanger until its temperature almost reaches the hot reservoir temperature. Ideally, the heat rejected per unit mass of refrigerant is:

$$q_{3-4} = h_3 - h_4 = C_p (T_3 - T_4) \quad . \quad (19)$$

The gas refrigerant then undergoes an isentropic expansion through a turbine. The temperature at the end of the expansion process is given by Eq. 17. The work extracted from the turbine per unit mass of refrigerant is

$$w_{4-1} = h_4 - h_1 = C_p (T_4 - T_1) \quad . \quad (20)$$

Because the turbine can be replaced by an expansion valve, the turbine work is not always available.

The refrigerant in this closed cycle undergoes continuous changes from States 1-2-3-4-1. The efficiency of refrigeration is given by the COP. For the Brayton cycle, with work available from a turbine, the COP is²²

$$COP_t = \frac{q_{1-2}}{w_{2-3} - w_{4-1}} = \frac{T_2 - T_1}{(T_3 - T_2) - (T_4 - T_1)} \quad . \quad (21)$$

For the Brayton cycle, with a throttling valve instead of a turbine, the COP is

$$COP_v = \frac{q_{1-2}}{w_{2-3}} = \frac{T_2 - T_1}{T_3 - T_2} \quad . \quad (22)$$

The total refrigeration capacity of the system depends on the quantity of refrigerant flowing in the cycle. The total heat absorbed and the total work input are then

$$\dot{Q}_{abs} = \dot{m} q_{1-2} \quad , \quad (23)$$

$$\dot{W}_{in} = \dot{m} w_{2-3} \quad . \quad (24)$$

This quantity of work input is increased by inefficiencies in the system, such as pressure drops in the piping, heat exchangers, compressor, and turbine. In addition, heat is transferred to the surroundings from the

compressor, turbine, and the heat exchangers. The actual net work input is given by²³

$$\dot{W}_{\text{act}} = \dot{m} \left[W_{2-3} - W_{4-1} \right] = \dot{m} \left[\frac{h_3 - h_2}{\eta_{\text{comp}}} - \eta_{\text{turb}} (h_4 - h_1) \right] . \quad (25)$$

From an energy balance on the system, the total heat rejected by the high-temperature heat exchanger must be the sum of the total heat absorbed, plus the net total work input, or

$$\dot{Q}_{\text{reject}} = \dot{Q}_{\text{abs}} + \dot{W}_{\text{act}} . \quad (26)$$

C. Component Sizing

The size or capacity of each component can be determined after the flow rate is known. The system piping diameter is determined using the conservation of mass law and a nominal gas velocity commonly used in heat exchanger design practice. The tubing diameter is given by

$$d = \left(\frac{4\dot{m}}{\pi \rho \bar{V}} \right)^{1/2} . \quad (27)$$

The minimum tubing thickness is specified using the highest temperature and pressure in the cycle and the pressurized piping standards, as stated previously.

The heat exchangers are sized using the theory and assumptions in Section IV.C. The high-temperature heat exchanger is similar to a gas-liquid, single-pass evaporator, because the liquid mass surrounding the heat exchanger is quite large compared with the gas flow rate and specific heat. Its temperature remains nearly constant. The low-temperature heat exchanger is a gas heat exchanger with flowing refrigerant inside the tubing and stagnant or natural convection in air on the outside. Consequently this exchanger has a lower overall heat transfer coefficient.

The pressure drops through the system can be estimated using the tubing diameters and the heat exchanger sizes, as discussed in Section IV.C. The

compressor and the expansion valve, or expander, are also specified using equations from Section IV.C.

D. Refrigerant Selection

A preliminary analysis was made using 10 candidate refrigerant gases operating through the Brayton cycle (Fig. 10). In each case, it was assumed that the refrigerant behaves as an ideal gas, that the specific heat is constant, and that the processes are reversible. Calculations were made to determine the cooling power, gas flow rate, work input for operation with a turbine and an expansion valve, and the corresponding COPs.

Results from the cycle calculations are shown in Table XIII. All of the inert gases with a specific heat ratio of 1.67 show that a compression ratio of 4 provides temperatures high and low enough for good approach at both heat exchangers. All the other gases require compression ratios considerably higher than 4 to provide adequate approach temperatures at either heat exchanger. From these results, helium and a mixture of helium and xenon were chosen as the two candidate refrigerants for which the remaining calculations were made.

E. Cycle Selection

A set of calculations were made for the Brayton cycle using efficiencies of 1 and less than 1.0. Power inputs were calculated using a turbine efficiency of 0.85 and a compressor efficiency of 0.86, which are best guesses for those components. The results are shown in Table XIV for an ideal case with perfect components and an "actual" case with more realistic component efficiencies. The comparison of COPs for the actual case, using a turbine and an expansion valve, shows that only by using the turbine can the Brayton cycle meet the design criteria established in an Section I, i.e., power input must be less than or equal to 22 W.

F. Flow Regime Selection

Figure 11 shows a plot of the relative heat transfer coefficients and the pressure drops for the inert gases and their binary mixtures operating in the laminar flow regime. Figure 12 shows the plots for turbulent flow conditions.²⁴ Operating a Brayton cycle in the turbulent regime would require use of a binary mixture of helium and xenon in any molecular weight

TABLE XIII
CANDIDATE REFRIGERANT GASES

Gas	m g/s	r P _H /P _L	P ₃ (atm)	T ₃ (°K)	COP	
					Valve	Turb
Helium ^a	2.75x10 ⁻²	4	4	696	0.189	1.40
Neon ^b	13.80x10 ⁻²	4	4	696	0.189	1.40
Argon ^c	27.50x10 ⁻²	4	4	696	0.189	1.40
Krypton ^d	57.60x10 ⁻²	4	4	696	0.189	1.40
Xenon ^d	90.40x10 ⁻²	4	4	696	0.189	1.40
Helium-Xenon ^d	17.16x10 ⁻²	4	4	696	0.189	1.40
Hydrogen ^b	9.78x10 ⁻²	6	6	674	0.159	1.416
Ammonia ^a	4.62x10 ⁻²	9	9	672	0.162	1.573
Methane ^a	7.90x10 ⁻²	9	9	677	0.166	1.484
Acetylene ^c	6.82x10 ⁻²	12	12	668	0.152	1.508

^aRef. 25.

^bRef. 26.

^cRef. 27.

^dRef. 24.

TABLE XIV
BRAYTON CYCLE REFRIGERATOR

	Ideal	Nonideal
Q _{cool}	8 W	8W
Flow Rate	2.75x10 ⁻² g/s	2.75x10 ⁻² g/s
P _{in} /Turbine	5.77 W	17.9 W
COP/Turbine	1.39	0.447
P _{in} /Valve	42.3 W	48.9 W
COP/Valve	0.189	0.164

(a) Relative Heat Transfer Coefficient

(b) Relative Pressure Drop

Fig. 11. Relative heat transfer coefficients and pressure drops for inert gases and their binary mixtures in laminar flow.

Fig. 12. Relative heat transfer coefficients and pressure drops for inert gases and their binary mixtures in turbulent flow.

from 15 to 45 to obtain the highest relative heat transfer coefficients. Operating a cycle in laminar flow would best be done using pure helium to get the highest relative heat transfer coefficients and the lowest relative pressure drops.

Two sets of calculations were made to size the components for a helium laminar flow cycle and a helium-xenon mixture, $MW=39.944$, flowing turbulently in the low-temperature heat exchanger. The component specifications for the pure helium cycle are given in Table XV and for the helium-xenon cycle in Table XVI. In both cases, the compressor and the turbine are the same size. The high-temperature heat exchanger was sized for internal laminar helium and helium-xenon flow and for natural convection to water outside the tubing. The low-temperature heat exchanger was sized for laminar flowing helium and turbulent flowing helium-xenon internally and natural convection to air on the outside tubing surface. A comparison of the components in both cycles is given in Table XVII.

The compressor and the turbine have the same volumetric flow rates in both cases. The tubing in the pure helium cycle is 1/2-in.-o.d., Schedule 40 Stainless Steel. The helium-xenon mixture cycle required 1/4-in.-o.d. high-pressure stainless steel tubing. The helium-xenon cycle require 2-1/4 times longer tubing for the high-temperature heat exchanger. This longer length can be arranged inside the pressure vessel wall and still be removed from the dewar and the electronics, so it does not represent any disadvantage. The low-temperature heat exchanger requires 2-1/8 times longer tubing for the helium-xenon cycle, but, because of the smaller diameter, it results in a wrapped tubing height 1/4-in. shorter than that for the pure helium cycle. Because the low-temperature heat exchanger tubing must reside inside the dewar and must surround the electronics to absorb its heat load, the tubing volume is an important parameter. The remaining diameter inside the low-temperature tubing is 1-1/2 in. for pure helium and 2 in. for the helium-xenon mixture, which gives an enclosed volume of 1-4/5 times larger for the helium-xenon case.

G. Conclusions

We concluded from the results of the above calculations that a Brayton cycle, using a mixture of helium and xenon with a molecular weight of

TABLE XV

BRAYTON CYCLE COMPONENTS; HELIUM, LAMINAR FLOW

Compressor	$\Delta p = 44 \text{ psig @ } \dot{q} = 0.477 \text{ ft}^3/\text{min}$ $r = 4, CF = 0.03$ $\eta_V = 0.961, \eta_{TOT} = 0.86$ $PD = 11.27 \text{ cm}^3/\text{rev @ } 1200 \text{ rpm}$
High Temperature	$U = 4.04 \text{ Btu/h-ft}^2\text{-}^\circ\text{F}$
Heat Exchanger	$\Delta T_{LM} = 66^\circ\text{F}$ $Q = 88.4 \text{ Btu/h over } A = 0.331 \text{ ft}^2$ Tube length = 68 in.
Turbine	$\Delta p = 44 \text{ psig @ } \dot{q} = 0.477 \text{ ft}^3/\text{min}$ $\eta_{\text{turbine}} = 0.85$
Low Temperature	$U = 0.805 \text{ Btu/h-ft}^2\text{-}^\circ\text{F}$
Heat Exchanger	$\Delta T_{LM} = 82^\circ\text{F}$ $Q = 27.3 \text{ Btu/h over } A = 0.414 \text{ ft}^2$ Tube length = 85 in.
Tubing	ASTM A-312 with welded connections $\sigma_{\text{allow}} = 14,300 \text{ psi @ } 850^\circ\text{F}$ $1/2\text{-in. o.d., } t_{\text{wall}} = 0.088 \text{ in.}$ $P_{\text{loss}} = 0.017 \text{ psig}$ 1.5-in.-i.d. electronics

TABLE XVI

BRAYTON CYCLE COMPONENTS: XE-HE, TURBULENT FLOW

Compressor	$\Delta p = 44 \text{ psig @ } \dot{q} = 0.477 \text{ ft}^3/\text{min}$ $r = 4, CF = 0.03$ $\eta_V = 0.961, \eta_{TOT} = 0.86$ $PD = 11.27 \text{ cm}^3/\text{rev @ } 1200 \text{ rpm}$
High Temperature	$U = 3.72 \text{ Btu/h-ft}^2\text{-}^\circ\text{F}$
Heat Exchanger	$\Delta T_{LM} = 66^\circ\text{F}$ $Q = 88.4 \text{ Btu/h, } A = 0.369 \text{ ft}^2$ Tube length = 154 in.
Turbine	$\Delta p = 44 \text{ psig @ } \dot{q} = 0.477 \text{ ft}^3/\text{min}$ $\eta_{\text{turbine}} = 0.85$
Low Temperature	$U = 0.766 \text{ Btu/h-ft}^2\text{-}^\circ\text{F}$
Heat Exchanger	$\Delta T_{LM} = 82^\circ\text{F}$ $Q = 27.3 \text{ Btu/h over } A = 0.436 \text{ ft}^2$ Tube length = 181 in.
Tubing	ASTM A-312 with welded connections $\sigma_{\text{allow}} = 14,300 \text{ psi @ } 850^\circ\text{F}$ $1/4\text{-in. o.d. } t_{\text{wall}} = 0.028 \text{ in.}$ $\Delta P_{\text{loss}} = 0.06 \text{ psig}$ 2.00-in.-i.d. electronics

TABLE XVII
BRAYTON CYCLE REFRIGERATOR COMPARISON

	<u>Helium</u>	<u>Xe-He</u>
Compressor	$\Delta p = 44 \text{ psig}$	$\Delta p = 44 \text{ psig}$
Turbine	$\Delta p = 44 \text{ psig}$	$\Delta p = 44 \text{ psig}$
<u>High-Temperature HX</u>		
Wraps	4	8
Height	2.16 in.	4 in.
Wall thickness	1/2-in. + t_{wall}	1/4-in. + t_{wall}
<u>Low-Temperature HX</u>		
Wraps	11	23
Height	6 in.	5.75-6 in.
Electronics	1.5-in. i.d.	2-in. i.d.
Volume of electronics	10.6 in. ³	18.85 in. ³
<u>Tubing</u>		
Outside diameter	0.54	0.25
Inside diameter	0.37	0.194

39.944, would be the best choice for a refrigerant gas. The cycle components include a single-stage turbine and compressor on the same shaft and a low-temperature heat exchanger and a high-temperature heat exchanger constructed from high-pressure stainless steel 1/4-in.-o.d. tubing. The low-temperature heat exchanger would operate in turbulent flow and the high-temperature heat exchanger would run in the laminar flow regime. The calculated input power is approximately 18 W for turbine and compressor efficiencies of 85% and 86%, respectively, which meets the criteria of being less than 22 W.

VI. JOULE-THOMPSON REFRIGERATION CYCLE

A. System

Refrigeration can be accomplished with the Joule-Thompson refrigeration cycle. This cycle is a gas cycle very similar to the Brayton cycle that uses a throttling valve in place of a turbine expander. The major components are shown in Fig. 13 and include a gas compressor, high-temperature heat exchanger, low-temperature heat exchanger, and throttling valve.

B. Theory

The Joule-Thompson refrigeration cycle schematic is shown in Fig. 14 and consists of two constant pressure processes, an isentropic compression, and isenthalpic expansion. The assumptions used in the preliminary analysis are as follows: (a) the processes are reversible, with the exception of the expansion through the throttling valve, and (b) the gas behaves as a compressible gas described by a compressibility factor. The theory for refrigeration is the same as the Brayton cycle, with the exception of the expansion process, which is isenthalpic rather than isentropic.

The Joule-Thompson cycle operates on the nonidealities of the refrigerant gases in the cycle. For an ideal gas, the derivative of temperature with respect to pressure is zero, but that same derivative is nonzero for real gases. The ratio is called the Joule-Thompson coefficient and is defined as:

$$\mu = (\partial T / \partial p)_{h=const} \quad (28)$$

Fig. 13. Joule-Thompson refrigeration cycle schematic.

Fig. 14. Temperature-entropy diagram for Joule-Thompson refrigeration cycle.

Fig. 15. Constant enthalpy lines.

Fig. 16. Inversion curve.

The ratio is positive for pressure drops that produce temperature decreases and is negative for pressure drops that produce temperature increases in an expanding gas. The plots of constant enthalpy lines for a gas shown on temperature and pressure axes are given in Fig. 15. The dotted line is the locus of points on the constant enthalpy curves for which the slope is zero (or the Joule-Thompson coefficient is zero). Expansions that occur to the left of the inversion curve produce temperature drops.

A general relation for the Joule-Thompson coefficient can be derived from the differential for enthalpy as

$$dh = c_p \cdot dT + [v - T(\gamma v / \gamma T)p] dp \quad . \quad 28 \quad (29)$$

Then, because the throttling process is isenthalpic, the ratio of temperature and pressure differentials becomes

$$\left(\frac{dT}{dp}\right)_h = \frac{1}{c_p} \left[T \left(\frac{dv}{dT}\right)_p - v \right] \quad . \quad (30)$$

For a gas that obeys the law

$$pv = ZRT \quad , \quad (31)$$

the total differential is given by

$$pdv + vdp = ZRdT + RTdZ \quad . \quad (32)$$

Solving for the ratio of the derivative of volume, with respect to pressure, gives

$$\left(\frac{dv}{dT}\right)_p = \frac{ZR}{p} + \left(\frac{RT}{p}\right) \left(\frac{dZ}{dT}\right) \quad , \quad (33)$$

which can be substituted into the relation for the Joule-Thompson coefficient to give

$$\mu = \frac{1}{c_p} \frac{RT^2}{p} \cdot \frac{dz}{dT} \quad .28 \quad (34)$$

This suggests that the plot of the compressibility coefficient could be used to determine the sign of the Joule-Thompson coefficient without very much more property data on any particular gas. Figure 16 shows a plot of the inversion line on reduced coordinates for pressure and temperature. Points that lie inside the curve have positive coefficients and can be used to provide reduced temperatures after a gas expansion.

Applying the information from the figure to this study would require that the critical temperature of a candidate refrigerant between the limits be

$$-154^{\circ}\text{C} < T_c < 573^{\circ}\text{C} \quad (35)$$

and that the high pressure from which the expansion takes place be between the limits, as in

$$1/2 < P_r < 11 \quad (36)$$

C. Refrigerant Selection.

Gases considered as candidates after a screening for suitable temperature limits are listed in Table XVIII. Examination of Eq. 34 shows that the sign of the Joule-Thompson coefficient is determined by the derivative of this compressibility coefficient with respect to temperature, but the magnitude depends upon both the state point and the ratio of the gas constant and the specific heat at constant pressure. Argon, xenon, krypton, propane, and carbon monoxide result in the largest ratios and are listed in descending order. Consideration of the required compression ratio to achieve acceptable approach temperatures, as in the Brayton cycle, results in compression ratio of 4, 4, 4, 6.4, and 6.95, respectively. Of these inert gases with small compression ratios and large R/c_p ratios, argon is the most favorable because it has the lowest pressure limit.

TABLE XVIII

JOULE-THOMPSON CANDIDATE REFRIGERANTS^a

Gas	R (KJ/Kg-K)	c _p (KJ/Kg-k)	T _c (K)	1/2 P _c (psia)	R/c _p
Ammonia, NH ₃	0.48822	2.060	405.5	818	.237
Argon, Ar	0.20813	0.5203	151.0	352	.400
Carbon dioxide, CO ₂	0.18892	0.8418	304.2	536	.224
Carbon Monoxide, CO	0.29683	1.0413	133.0	253	.285
Krypton, Kr	0.09922	0.251	209.4	399	.395
Methane, CH ₄	0.51835	2.254	191.1	337	.229
Nitrogen, N ₂	0.29680	1.042	133.0	246	.284
Propene, C ₃ H ₆	0.19758	0.665	365.0	335	.297
Sulfur dioxide, SO ₂	0.12978	0.632	430.7	572	.205
Xenon, Xe	0.06332	0.159	289.8	427	.398

^aRef. 28.

Preliminary calculations for a Joule-Thompson cycle using an argon refrigerant were made. The mass flow rate was determined by considering the maximum power input for this system and the temperature change produced by the compression step in this cycle. The calculated flow rate is only 52% of the flow required to absorb the heat exchanged in the low temperature heat exchanger. An isenthelpic expansion between the states established for this cycle result in a very small (4 K) temperature change, which is only 1-1/2% of the required temperature change used to complete a refrigeration cycle.

For all of the reasons stated above, argon is not feasible as a refrigerant in a Joule-Thompson cycle designed to operate at the conditions required for this study.

VII. ACOUSTICAL REFRIGERATION

A. Background

Thermal acoustic effects were first noted by glassblowers. The sounds produced by these craftsmen were the result of a large temperature gradient between the mouthpiece and the bulb of the glass blowing tool.²⁹ Rayleigh gives examples of sound-produced vibrations of a gas column in a hollow tube with an established temperature gradient. He describes experiments by Rijke in which a fine metallic gauze was stretched across the bottom end of an open pipe that was then heated with a gas flame. The pipe begins emitting a sound about a second after the flame is removed and "rises to such an intensity as to shake the room, after which it gradually dies away."

In 1943, a similar phenomenon was described by Taconis³⁰ during his cryogenic experiments. He observed that a vibration might occur in a gas column if the temperature gradient along the column was large enough (room temperature at one end and -269°C at the other end). Then, in 1949, there was an attempt to determine the explanation for the spontaneous vibrations.³¹ Kramer's analysis was the first quantitative calculation of thermally driven acoustic oscillations. In the late 1960s, N. Rott wrote a series of papers in which he attempted to improve and extend Kramer's analysis so that it would agree with experimental observations. Rott's work is based upon the fundamental equations of thermodynamics and fluid

mechanics of this phenomenon and is an effort to determine what causes the gas column to become unstable.³²

In the cryogenic research field, there were some parallel efforts made to use this phenomenon for refrigeration purposes by providing a forced oscillation of a gas column in a hollow tube. In 1959, McMahon and Gifford³³ described a pulse tube gas refrigerator that maintained a 220°C temperature differential while removing 82 W of refrigeration load. Then in 1963, Gifford and Longworth³⁴⁻³⁶ described a refrigerator in which the displacer piston had been omitted and had been replaced by a "gas piston." Experimental results of their work demonstrated that significant temperature ratios could be achieved by using multiple stages of acoustic pulse tubes and regenerators. Then, in 1966, Colangelo and Fitzpatrick published an analysis of the system based on the conservation equations applied to each section of the refrigerator system.³⁷

B. System

Refrigeration can be accomplished using a fluid refrigerant, without relying on its phase changes or on the Joule-Thompson effect. Acoustic refrigeration is the result of both an enthalpy pumping process and a surface heat pumping process. The thermodynamic cycle described will be referred to as the Surface Heat Pumping Cycle (SHP)³⁶ and the apparatus in which it occurs as a Pulse Tube Refrigerator (PTR). The PTR, shown schematically in Fig. 17,³⁷ consists of a compressor with a high- and a low-pressure reservoir, inlet and exhaust valves, a thermal regenerator, and a hollow pulse tube with a heat exchanger at its closed end. Refrigeration is available at the junction between the regenerator and the pulse tube, which is the coldest point in the system.

The inlet and exhaust valves regulate the flow of refrigerant into and out of the system. The regenerator is a heat exchanger operating on a cyclic basis, cooling the gas from its inlet temperature to the load temperature during the inlet phase and reheating the expanding refrigerant almost to the inlet temperature during the exhaust phase. The regenerator matrix material is a high-density, high-specific heat material that serves as one end of a cold sink. The screens at the ends of both the pulse tube and the regenerator are intended as flow straighteners. The pulse tube is a

long hollow tube with the flow straighteners at its open end and a heat exchanger at its closed end. The open end of the pulse tube is the other end of the cold sink. The refrigerator, or the refrigeration load, is located between the regenerator and the pulse tube. The heat exchanger at the closed end of the pulse tube provides for the heat rejection from the system to the cooling medium. In effect, this apparatus transfers heat from the inlet/exhaust valve end of the regenerator to the heat exchanger at the closed end of the pulse tube by a surface heat pumping process and by an enthalpy pumping process.

Refrigeration with this system is referred to as "acoustical," primarily because it involves a gaseous medium subjected to cyclic pressure changes at frequencies that are audible to the human ear.

C. Theory

The SHP cycle is shown in Fig. 18³⁶ on temperature-entropy axes along with the Carnot cycle and the Brayton cycle. The Carnot cycle is described by state points from 1-2'-3-4'-1 which include two isothermal heat exchange processes and an isentropic expansion and an compression process. The Brayton cycle is described by the state points from 1-2"-3-4"-1, and includes two constant pressure heat exchange processes and an isentropic expansion and a compression process. The SHP cycle fits inside the Brayton envelope and is described by the state points from 1-2-3-4-1. This cycle has two constant pressure heat exchange processes and two polytropic expansion and compression processes.

The COP for this cycle is given by

$$\text{COP} = \frac{Q_{\text{absorbed}}}{W_{\text{input}}} . \quad (37)$$

This cycle is more efficient than the Brayton Cycle, partly because the heat transfer that occurs during each complete cycle occurs continuously and is not confined to a particular branch of the cycle. Irreversibilities from gas flow through the valves, heat transfer across finite temperature differences, and extra gas volumes (other than the gas in the pulse tube) contribute to the inefficiencies of the cycle. The COP for an ideal Carnot cycle refrigerator is

$$\text{COP}_c = Q/W_c = \frac{T_c}{T_w - T_c} \quad (38)$$

An intrinsic COP for the SHP cycle with the finite temperature difference necessary for heat transfer is defined by

$$\text{COP}_{\Delta T} = \frac{T_c - \Delta T}{T_w + \Delta T - (T_c - \Delta T)} = \frac{T_c - \Delta T}{(T_w - T_c + 2\Delta T)} \quad (39)$$

Then the thermal efficiency of the SHP refrigeration cycle as compared with the Carnot cycle is

$$n = \frac{\text{COP}_{\Delta T}}{\text{COP}_c} = \frac{(T_w - T_c)(T_c - \Delta T)}{T_c(T_w - T_c + 2\Delta T)} \quad (40)$$

The total efficiency is lower if the inefficiencies in the operation of each component are quantified and accounted for.

The SHP cycle is best understood by considering a mass of gas in a closed, hollow tube subjected to cyclic pressure variations. If these variations result from the delivery of gas from a single point (Fig. 19), a large temperature gradient can be established. The small gas mass at X' has temperature T1'. Pressure in the long tube increases because of the constant temperature gas flowing in from the left, which displaces the mass to X". For this polytropic compression process, the relationship between temperature and pressure is

$$\frac{T''}{T'} = \left(\frac{P''}{P'} \right)^{\frac{n-1}{n}}, \quad (41)$$

where n = polytropic coefficient,

T' = gas temperature at X',
 T'' = gas temperature at X",
 P' = gas pressure at X', and
 P'' = gas pressure at X" .

Fig. 18. Surface heat pumping cycle comparison with the Carnot and Brayton cycles.

Fig. 19. Temperature and displacement history of small gas mass δm at X^I .

After the compression process the gas parcel temperature is T_1'' . Then, if the pressure is momentarily held constant at P'' , the gas at X'' transfers heat to the wall by conduction, because its temperature, T_1'' , is higher than that of the adjacent wall. After this heat transfer process, the gas at X'' has a temperature T_2'' . Then the pressure in the tube is released, allowing gas to flow out of the tube to the left and causing it to expand and cool. This expansion displaces the mass back to X' and cools it to T_2' , which is slightly below the temperature of the tube wall at X' . Again, if the pressure is momentarily held constant at P' , the gas receives heat from the wall by conduction. This process is plotted in Fig. 20 and shows both the gas temperature and the tube wall temperature as a function of position. In this figure, the enthalpy pumping portion of the cycle occurs between points X' and X'' , and the surface heat pumping occurs during the intervals of time that the gas mass resides at either X' or X'' . Both processes result in a net transfer of enthalpy and heat from left to the right or toward the closed end of the hollow tube. The finite time interval required to allow surface heat pumping to occur implies that the compression and expansion processes must be slow enough to allow heat transfer; therefore, they must be polytropic rather than isentropic. In this manner, a large temperature gradient can be established between the ends of the pulse tube.

If the assumptions are that the refrigerant gas is a perfect gas and that fluid flow in the pulse tube is both laminar and planar in a constant area tube, then a relationship for temperature as a function of position in the pulse tube is

$$\frac{T''}{T'} = \frac{X'}{X''}^{n-1} \quad (42)$$

This can be further extended by considering the volume ratios of refrigerant gas in the heat exchanger at the closed end of the pulse tube and the gas volume of the pulse tube as

$$\frac{T_h}{T_x} = \left(\frac{V_{pt}/V_h + n - 1}{n} \right)^{n-1} \quad (43)$$

where T_h = gas temperature in the heat exchanger,
 T_x = gas temperature at x ,
 V_{pt} = pulse tube volume,
 V_h = heat exchanger gas volume, and
 n = polytropic coefficient.

This SHP cycle will establish a steady state temperature difference as large as the polytropic pressure-temperature relationship allows.

It has already been noted that the compression and expansion process must be polytropic rather than isentropic. Heat transferred during a cycle requires a minimum finite time interval. If the interval is too short, the process approaches isentropic conditions and no surface heat pumping can occur. At the other extreme, the interval may be too long, during which heat transfer is completed and nothing else occurs. Assuming that each heat transfer process occurs at constant pressure, each process can be described by the conduction equation as

$$\frac{\partial T}{\partial t} = \left(\frac{1}{V^2} \frac{\partial^2 T}{\partial x^2} \right) \quad (44)$$

Then the temperature of a control volume at any instant depends on its location in the tube and on the properties of the gas refrigerant. This equation is nondimensionalized by introducing the pulse rate, N , the inside diameter of the pulse tube, D , the length of the tube, L , a reference temperature, T_c , and a reference thermal diffusivity, α_c , evaluated at T_c . The parameters are

$$\tau^* = tN, \quad X^* = \frac{X}{L}, \quad D^* = \frac{D}{L}, \quad \alpha^* = \frac{\alpha}{\alpha_c}, \quad T^* = \frac{T - T_c}{T_c} \quad (45)$$

The nondimensionalized heat conduction equation is then

$$\frac{\partial T^*}{\partial \tau^*} = \left(\frac{\alpha_c}{ND^2} \right) \frac{\partial^2 T^*}{\partial X^{*2}} \quad (46)$$

This heat transfer is assumed to take place radially in the pulse tube with little or none occurring axially or angularly.

The heat transfer processes that occur in the regenerator and in the hot end heat exchanger are cyclic as opposed to the conventional steady-flow, unidirectional processes. The analysis and theory for conventional heat exchanger design apply to these components, but the transient equations must also be considered.

A plot of the gas temperature as a function of position in the refrigerator system is shown in Fig. 21.³⁵ As the gas enters the system, the regenerator precools it from T_w to T_c . This portion of the temperature profile is linear, which reflects the large thermal mass of the regenerator and the linear nature of the heat transfer between the gas and the matrix. The gas temperature rises nonlinearly in the pulse tube to a maximum temperature T_m , with the shape of the curve reflecting the polytropic compression. In the hot end heat exchanger, the gas temperature drops to T_h , which is assumed to be uniform along the length of the heat exchanger. This implies that "perfect" heat transfer occurs in the heat exchanger. The heat rejected to the cooling medium is then

$$\dot{Q}_{rej} = \dot{M}_h C_p (T_m - T_h) \quad , \quad (47)$$

where $\dot{M}_h$ = mass flow rate at heat exchanger,

T_m = maximum gas temperature, and

T_h = gas temperature in heat exchanger.

During the expansion process, the gas cools from T_h to T_e , which is slightly cooler than the entering gas temperature. This results in a refrigeration effect at the junction between the regenerator and the pulse tube, which is given by

$$\dot{Q}_{refrig} = \dot{M}_c C_p (T_c - T_e) \quad , \quad (48)$$

where $\dot{M}_c$ = mass flow rate at $x=0$,

T_c = inlet gas temperature at pulse tube entrance, and

T_e = exit gas temperature at pulse tube entrance.

The gas then passes back through the regenerator, which reheats it to a temperature slightly less than that when it entered the regenerator. The

Fig. 20. Gas and wall temperature vs position during a surface heating pumping cycle.

Fig. 21. Pulse tube with filling and exhausting temperature pattern.

Fig. 22. Control volume in the refrigerator.

gas recycles back to the low-pressure reservoir, through the compressor, and then to the high-pressure reservoir to repeat the cycle.

D. Component Sizing

The size or capacity of each component in the system can be determined if the flow rate is known. The flow rate in this system is not a constant; it varies with time and position. If the entire pulse tube system of gas is considered as a control volume, then the energy balance at steady state conditions for a single cycle of length τ is

$$\tau_c C_p (\dot{M}_c T_{gc})_w + \dot{Q}_{\text{heater}} \tau + \dot{Q}_{\text{leak}} \tau + \tau_e C_p (\dot{M}_e T_{ge})_w - \dot{Q}_H \tau = 0 \quad , \quad (49)$$

where τ_c, τ_e = compression or expansion cycle times,

$\dot{M}_c, \dot{M}_e$ = mass flow rate at regenerator entrance during
during compression or expansion,

T_{gc}, T_{ge} = gas temperatures during compression, expansion,

$\dot{Q}_{\text{heater}}$ = refrigeration load,

$\dot{Q}_{\text{leak}}$ = heat leak into control volume,

$\dot{Q}_H$ = heat rejected from heat exchanger,

w = subscript refers to warm end of regenerator.

If the assumption is made that the compression and expansion portions of the cycle are the same, then

$$\tau_c = \tau_e = \psi \tau \quad , \quad (50)$$

where ψ = fraction of total cycle time.

Then the energy balance reduces to

$$\psi C_p \dot{m} (T_{gc} - T_{ge})_w + \dot{Q}_{\text{heater}} + \dot{Q}_{\text{leak}} + \dot{Q}_H = 0 \quad . \quad (51)$$

The quantity $\dot{Q}_{\text{heater}}$ represents the imposed refrigeration load placed between the pulse tube and the regenerator. This heat transfer would most practically occur by conduction, from the warm refrigerator to the cold end of the pulse tube. In this manner, the gas volume undergoing pressurization

would be minimized and the laminar, plane flow pattern in the pulse tube would remain undisturbed. The refrigeration load could be limited by the geometry, material used at the interface, or the approach temperature as given by

$$\dot{Q}_{\text{heater}} = UA (T_r - T_c) \quad (52)$$

where T_r = temperature in refrigerated section,

U, A = as previously defined in Eq. 9.

If heat pipes were used, then a smaller approach temperature is possible.

The quantity $\dot{Q}_{\text{leaks}}$ represents any radiation, conduction, or convection heat leaks into the system. This quantity depends partly upon the steady state temperature difference and upon the degree of insulation used. The quantity $C_p[\dot{m}(T_{g_c} - T_{g_e})w]$ represents the difference in the enthalpy flux at the valve end of the regenerator. It can be used in conjunction with the polytropic temperature-pressure relationship to determine the size of the compressor. The compressor must be capable of a compression ratio

$$r = \frac{P_H}{P_L} \quad , \quad (53)$$

at a predetermined P_L which should be slightly higher than ambient pressure. The flow rate is not known at this point but can be determined in the analysis of the regenerator.

The quantity $\dot{Q}_h$ represents the reject heat that must be transferred from the hot end heat exchanger to the cooling medium. $\dot{Q}_h$ is the sum of the refrigerator load, all the heat leaks, and the difference in the enthalpy flux. The minimum heat transfer area, with some possible modifications for its cyclic operation, is determined using the theory and equations stated in Section IV.C. After establishing the required heat transfer area, the gas volume in the heat exchanger, V_h , is known and can be used to determine the gas volume of the pulse tube. Knowing the volumes of both the pulse tube and the heat exchanger at its hot end, the geometry

can be fixed by selecting either the tube length or its diameter. For practical reasons, either variable may be constrained.

To scope the size of the regenerator, the conservation equations applied to a control volume across the regenerator must be solved. The control volume and its pertinent parameters are shown in Fig. 22. The energy balance for gas flowing through the regenerator is³⁷

$$C_p \frac{\partial}{\partial x} \left(\dot{M} T_g \right) - K_g A_o \frac{\partial^2 T}{\partial x^2} + h_T A_T (T_g - T) + \frac{C_v A_o}{R} \left(\frac{\partial p}{\partial t} \right) = 0 , \quad (54)$$

where T_g = gas temperature,

T = matrix temperature,

K_g = gas conductivity,

A_o = regenerator cross-sectional flow area,

h_T = regenerator heat transfer coefficient,

A_T = regenerator heat transfer area,

p = gas pressure, and

t = time.

C_p , C_v = constant pressure, volume specific heat of the gas

The first term represents the change in enthalpy flux across the control volume, the second term gives the energy exchange from conduction between the gas and the matrix material, the third term gives the energy exchange between gas and matrix provided by convection, and the last term represents the work of compression. The energy equation written for the matrix is³⁷

$$K_m A_o \frac{\partial^2 T}{\partial x^2} + h_T A_T (T_g - T) = M c_m \frac{\partial T}{\partial t} , \quad (55)$$

where K_m = conductivity of the matrix material,

M = mass of the matrix material, and

c_m = specific heat of the matrix material.

The first term represents the conduction and the second term is the convection heat transfer between the gas and the matrix material. These terms are equal to the rate of change of energy of the matrix.

Assuming that the gas refrigerant is a perfect gas, the conservation of mass equation is derived from $pV = mRT$:³⁷

$$\frac{\partial \dot{m}}{\partial x} = \frac{-A_0}{R} \frac{\partial}{\partial t} \left(\frac{P}{T_g} \right) \quad (56)$$

The boundary conditions on this system of equations are

$$\begin{aligned} \text{at } x = 0: \quad \dot{m} &= \dot{m} \quad (t) \\ T_g &= T_g \quad (t) \\ \text{at } x = 1: \quad T &= T_{gw} \quad (t). \end{aligned} \quad (57)$$

Solution of this system of partial differential equations establishes the quantities T , T_g , and $\dot{m}$ as functions of x and time. Thus, the size of the regenerator can be determined for a specified rate of the work of compression, and the compressor can be specified once the bounds on $\dot{m}$ are known.

E. Preliminary Analysis

A preliminary analysis of the SHP cycle was made using helium as the refrigerant. The assumptions used in the analysis include: (1) helium behaves as a perfect gas, (2) there is plane, laminar flow in the pulse tube, (3) there is perfect heat transfer in the hot end heat exchanger, and (4) the device delivers no mechanical work, but rejects heat and enthalpy in the form of heat.

Experimental and theoretical results from the reference by Colangelo and Fitzpatrick,³⁷ with the same temperature ratio and different pressure ratios at a given pulse rate, were used as the basis for the calculation of the refrigeration possible at the conditions pertinent to this study. Table XIX lists the parameters of the Colangelo and Fitzpatrick system and parameters for this study for two experiments with different average pressures and pressure differences. Both cases used a pulse rate of 158 reversals/minute. The average pressure and the maximum pressure difference for Experiments 3-4 and 3-5 are $P_{avg} = 64$ psia and 82 psia and $\Delta P = 72$ psi and 90 psi, respectively.

TABLE XIX
PULSE TUBE REFRIGERATOR PARAMETERS

A. Predicted

	<u>MIT</u>	<u>This Study</u>
V_R , Regenerator Gas Volume	3.27 in. ³	6.95 in. ³
V_{PT} , Pulse Tube Volume	3.39 in. ³	7.21 in. ³
V_H , Heat Exchanger Gas Volume	0.673 in. ³	1.43 in. ³
V_{PT}/V_H	5.04	5.04
V_R/V_H	0.964	0.964
ϵ_R , Regenerator Void Fraction	0.388	0.388
ϵ_{PT} , Pulse Tube Void Fraction	1.00	1.00
T_C , Cold End Temperature	362.2°R	423K = 761.4°R
T_H , Hot End Temperature	507.7°R	593K = 1067.4°F
T_C/T_H	0.715	0.713

B. Experimental

	MIT Measured $\dot{Q}$ <u>heater</u>	MIT Calculated $\dot{Q}$ <u>heater</u>	This Study w/MIT Refrigerator $\dot{Q}$ <u>heater</u>	This Study w/enlarged Refrigerator
Case 3-4	10.0 W	14.7 W	7.12 W	14.7 W
Case 3-5	15.5 W	17.9 W	8.74 W	17.9 W

The results show that operation at either pressure ratio would provide sufficient refrigeration, with Experiments 3-5 providing slightly more than the 8 W specified using the same apparatus as in the reference. Both experiments would provide more than the specified load for a scaled-up refrigerator volume and pulse tube volume.

F. Conclusions

The SHP cycle is an attractive idea for refrigeration because it is slightly more efficient than the Brayton cycle operating between the same conditions. The apparatus described above is capable of removing the specified refrigeration load at the temperatures pertinent to this study. The size of the required pressure reservoirs and the compressor remains undetermined.

VIII. ABSORPTION REFRIGERATION CYCLE

A. Background

Refrigeration can be accomplished without supplying high-grade energy to a compressor in a mechanical refrigeration cycle. The absorption refrigeration cycle uses low-grade heat in the form of a heat engine to replace the compressor in a vapor compression cycle.³⁸

A French engineer, Ferdinand C.P. Carre, invented the absorption cycle in Paris, France, in 1850.³⁹ The absorption cycle operates on the distillation principle to separate a rich solution of solvent-solute into two flow streams: (1) a liquid absorbent, or the "weak solution," used for recovering and recycling the refrigerant, and (2) a liquid solute or "strong solution," which is recycled as the refrigerant. This cycle can be driven by waste heat or by any available heat source with a temperature high enough to drive the distillation process.

The most common commercial absorption refrigeration system is a binary system of water and ammonia in which water is the absorbent and ammonia is the refrigerant. Other commercial systems use water and lithium bromide with LiBr as the refrigerant and a combination of Freon-22 and DMF with Freon-22 as the refrigerant.³⁹ Current literature and sources of thermodynamic data concerning absorption refrigeration cycles other than those stated above are sparse when compared with the body of literature

available for the material properties and the design and analysis of mechanical refrigeration cycles. A recent computerized search of the literature since 1971 revealed that most of the work done in the field concerned the search for binary solution systems suitable for use in an absorption cycle.

B. Theory

The major components of the absorption refrigeration cycle are shown schematically in Fig. 23 and include a gas refrigerant condenser, a throttling valve, an evaporator, an absorber, a liquid pump, a regenerator, and a solution heat exchanger.³⁹ The left side of the schematic includes the condenser, throttling valve, and the evaporator that operate on the pure refrigerant in the same manner as a vapor compression cycle. The right side of the schematic represents the heat engine used to replace the compressor. These components operate on the binary solute-solvent pair to alternately combine and separate the solute gas from the solvent carrier. The cycle can operate only on a solution system that is not azeotropic. The schematic further divides the components by the pressure at which they operate, with the solution heat exchanger, regenerator, and condenser operating at the high-level condenser pressure. The evaporator and the absorber operate at the evaporator pressure or the low-level pressure. The solution pump provides the pressure increase required for the refrigerant stream to flow from the absorber to the regenerator, and the throttling valve provides the expansion from high- to low-pressure levels in the cycle.

The evaporator is a steady-flow open system component with a single fluid stream of fixed concentration. The mass balance and the concentrations are as follows:

$$\begin{aligned} \text{Mass:} \quad & \text{Vapor}_{\text{out}} = \text{Refrigerant}_{\text{in}} \\ \text{Concentration:} \quad & Y_e = X_r \end{aligned} \quad (58)$$

The heat absorbed by the evaporator is

Fig. 23. Absorption refrigeration cycle.

$$Q_e = V(H_i - h_r) \quad .^{39} \quad (59)$$

The operating pressure in the evaporator depends upon the specified temperature. Because there are pressure drops between the evaporator and the absorber, the refrigerant vapor pressure must be high enough to move vapor to the absorber. The absorber is primarily a heat exchanger with a main purpose of cooling the feed gas and condensing it completely. The absorber operates at a slightly lower pressure than does the evaporator, and it combines the "weak solution" absorbent with the pure gas refrigerant into a "strong solution." This absorption process is endothermic and releases the "heat of solution" per unit mass of flowing "strong solution." Figure 24 illustrates each flow stream and its relevant properties. The total mass and the refrigerant mass balances are given by

$$\begin{aligned} \text{Mass:} \quad & V_i + L_i = L_o \\ \text{Concentration:} \quad & V_i Y_i + L_i X_i = L_o X_o \quad .^{39} \end{aligned} \quad (60)$$

The "heat of solution" released is:

$$Q_a = L_o (H_m - h_o) \quad ,^{39} \quad (61)$$

which must be rejected to the surroundings.

The strong solution then passes through the liquid pump, raising its pressure to slightly above that of the regenerator. In most applications, the fluid streams between the regenerator and the absorber pass through a solution heat exchanger to preheat the strong solution and to cool the weak solution, thereby reducing the amount of heat input necessary to the regenerator.

The strong solution entering the regenerator is further heated to separate the gas refrigerant dissolved in the strong solution into a weak solution and a refrigerant vapor stream. This distillation is accomplished

Fig. 24. Absorber schematic.

Fig. 25. Basic distillation regenerator.

in a series of partial vaporization and condensation steps along the length of the distillation column. Figure 25 is a schematic of a basic distillation unit, or a regenerator, illustrating each flow stream and its properties. Both a concentration and a temperature gradient exist along the length of the regenerator. The heat input at the bottom through the reboiler is transmitted to the top of the column in a plate-by-plate sequence because of the temperature differences. Because continuous distillation requires a volatile liquid, a reflux liquid is supplied from the condenser to the top of the column to keep the plates wet. The overall mass balance and a refrigerant mass balance are given by

$$\begin{aligned} \text{Mass:} \quad & F = R + L_w \\ \text{Concentration:} \quad & Fx_f = Rx_r + L_w X_w \end{aligned} \quad (62)$$

A heat balance of the subsystem is

$$FH_f + Q_r = Rh_r + L_w h_w + Q_c \quad .^{39} \quad (63)$$

Note that Q_r is the heat energy used to drive the distillation process and must be available at the highest temperature of the solution in the column. The heat rejected by the condenser is Q_c . It is included in the regenerator subsystem to ensure that a steady stream of liquid refrigerant is fed to the top of the regenerator. This fluid stream is the "reflux." The material leaving the condenser or its refrigerant holding drum is a completely condensed distillate.

The condenser operates at a slightly lower pressure than does the regenerator. This pressure corresponds to the temperature at which the refrigerant condenses. Flow through the condenser occurs at a fixed-refrigerant concentration. The mass balance is given by

$$V_r = L_r + R \quad . \quad (64)$$

The heat rejected is given by

$$Q_c = V_r(H_r - h_r) \quad .^{39} \quad (65)$$

An energy balance on the entire cycle operating at steady state is given by

$$Q_e + Q_r + W_p = - Q_c - Q_a \quad . \quad (66)$$

The quantity Q_e represents the refrigeration capacity or "cooling effect," Q_r represents the required inlet heat necessary for distillation, W_p is the electrical energy necessary to operate the pumps, Q_c is the heat rejected by the condenser, and Q_a represents the heat rejected by the absorber. The quantity Q_r can be minimized by the use of a solution heat exchanger, which in turn reduces the quantity Q_c . The minimum value of Q_r would correspond to Carnot cycle efficiency of both the refrigerator on the left side of the cycle schematic and Carnot efficiency for the heat engine that replaces the compressor. This minimum Q_r is

$$Q_r = Q_e \cdot \frac{T_r}{T_r - T_c} \cdot \frac{T_c - T_e}{T_e} \quad .^{38} \quad (67)$$

The total cycle refrigeration capacity depends upon the quantity of flowing refrigerant and is given by

$$V = R = Q_e / (H_e - h_r) \quad . \quad (68)$$

The efficiency of this refrigeration cycle is also described by the COP as

$$COP = Q_e / (Q_r + W_p) \quad . \quad (69)$$

An estimate of the maximum COP, ignoring the pump work, can be obtained by rearranging the above equation into the form

$$\text{COP}_{\max} < \frac{Q_e}{Q_r} = \frac{T_e}{T_c - T_e} \cdot \frac{T_r - T_c}{T_r} \quad 40 \quad (70)$$

C. Component Sizing

The size or capacity of each component can be determined after the composition and mass flow rate of each fluid stream are known. System tubing is designed as discussed previously. The condenser, evaporator, and solution heat exchanger are designed using the equations and assumptions stated previously. The solution pump, reflux pump, and the throttling valve are sized to raise or lower the pressure of a given fluid stream by the amount specified at the given flow rate. The refrigerant-holding drum is sized based on the reflux flow rate and a prespecified hold-up time.

The absorber is primarily a heat exchanger designed using the equations and assumptions stated in Section IV.C. The heat of solution released during the absorption process determines the heat exchange area. The inlet gas flow rate and a prespecified hold-up time determines the head room required above the heat exchanger tubes, and the net liquid flow rate fixes the size of the shell.

The regenerator is designed based upon the overall heat and mass balances stated above. A more detailed examination of the distillation process specifies the number of distillation trays or stages necessary between the specified inlet and outlet flow streams. The enthalpy and concentration point for each flow stream can be plotted on an enthalpy-concentration diagram drawn for a specified operating pressure.

Figure 26 shows a detailed schematic of flow streams in the upper or "rectifying section" of the regenerator. The total mass balance and a refrigerant mass balance for the upper section are

$$\begin{aligned} \text{Mass:} \quad & V_{n+1} = L_n + R \\ \text{Concentration:} \quad & \left(V_{n+1} \right) \left(Y_{n+1} \right) = L_n X_n + R x_r \end{aligned} \quad (71)$$

The heat balance is

$$V_{n+1} H_{n+1} = L_n H_n + R h_r + Q_c \quad (72)$$

After some algebraic manipulation, the equations can be rearranged as mass, concentration, and heat ratios in the form

$$\frac{V_{n+1}}{R} = \frac{X_r - X_n}{y_{n+1} - X_n} = \frac{A_c - h_n}{H_{n+1} - h_n}, \quad (73)$$

where $A_c = h_r + Q_c/R$.

The points for $x = 1, 2, 3, \dots$ to n can be plotted to construct a Ponchon Diagram of the rectifying section, as shown in Fig. 27. Point (A_c, X_r) , the internal reflux ratio at the liquid concentration x_l , is plotted and used as the "upper swing point" for each operating line of the rectifier. The first operating line is a vertical line drawn from the x -axis to the point (A_c, X_r) . Its intersection with the saturated vapor line establishes the point y_1 , the vapor concentration. A constant temperature line, or a tie-line, drawn through y_1 , establishes point x_1 . A second operating line is drawn between x_1 and A_c , thus establishing point y_2 , and so on for sufficient stages of distillation until the concentration at the feed inlet is reached. The sum of complete and any fractional Ponchon operating lines determines the number of trays or distillation stages above the feed inlet point.

The lower section of the regenerator is designed in a similar fashion. Figure 28 shows a detailed mass balance diagram of the lower or "stripping section" of the regenerator. The total mass balance and the refrigerant mass balance for this section are given by

$$\begin{aligned} \text{Mass:} \quad & V_m + L_m = L_{m+1} \\ \text{Refrigerant Mass:} \quad & V_m Y_{m+1} + L_m X_m = L_{m+1} X_{m+1} \end{aligned} \quad (74)$$

The heat balance on the lower section, including the reboiler, is

$$V_m H_m + L_w H_w = L_{m+1} h_{m+1} + Q_r \quad (75)$$

Algebraically rearranging these equations into mass, concentration, and heat ratios gives

$$\frac{V_m}{L_w} = \frac{X_{m+1} - X_w}{Y_m - X_{m+1}} = \frac{h_{m+1} - A_w}{H_m - h_{m+1}}, \quad (76)$$

where $A_w = h_w - Q_r/L_w$.

The point (A_w, x_w) is plotted on the enthalpy-concentration diagram and is used as the "lower swing point" for each operating line between the feed inlet and the liquid "weak solution" outlet point. The same process is repeated, drawing successive operating lines to locate successive x_m points, from which the constant temperature tie lines are drawn to establish y_m points, until the feed inlet concentration is reached. The required number of trays is given by the sum of complete plus fractional operating lines between the lower swing point and the feed input point. The regenerator tank must be large enough to accommodate the total number of distillation sections, plus a specified quantity of weak solution, and also have head room enough for the overhead vapor. The heat exchange at each stage is determined from the temperatures, enthalpies, and concentrations given by the Ponchon diagram. Each section is then a heat exchanger that is designed using the equations and assumptions stated previously, with appropriate film coefficients for evaporation.

The reboiler heat exchanger is designed using the assumptions and equations stated previously.

D. Preliminary Analysis

A preliminary analysis of an absorption refrigeration system could not be made for the typical commercial solute-solvent combinations because the temperature range specified in Section I is above the critical temperature of all the common solute gases.

The most common solute gas, ammonia, has a critical temperature of 133°C at 300 psia, which is even below the specified cold reservoir temperature. Its temperature range at 300 psia is 50°C < T < 214° C. Lithium bromide systems have a refrigerant operating range of -18°C < T < 110°C and a solution temperature range of 4°C < T < 177°C. Other binary systems that use the fluorocarbon gases as a refrigerant are also limited to relatively low temperatures. Table XX lists candidate absorption refrigerants and their critical properties.

Fig. 28. Mass balance diagram of the regenerator stripping section.

TABLE XX
ABSORPTION GAS PROPERTIES^a

Gas	Formula	Mol Mass	γ c_p/c_v	Critical		
				$P(\text{bars})$	$T(^{\circ}\text{K})$	$(^{\circ}\text{C})$
n-Decane	$\text{C}_{10}\text{H}_{22}$	142.28	1.03	22.1	619.4	346
n-Nonane	C_9H_{20}	128.25	1.04	23.8	596.1	323
n-Octane	C_8H_{18}	114.22	1.05	25.0	569.4	296
Water Vapor	H_2O	18.02	1.33	221.2	647.8	375

^aRef. 39.

E. Literature Search

An extensive literature search was made in an effort to locate a suitable absorbent-refrigerant mixture for use between 150°C and 320°C. The following data bases were searched: Inspec, NTIS, Compendex, and CA Search of the American Chemical Society. Several survey articles were found, including an article discussing methods for developing usable absorbent-refrigerant mixtures.

The avenues of research available for identifying a suitable absorbent-refrigerant pair include using additives with existing fluids, modifying existing fluids, screening fluids, and synthesizing new fluids.⁴¹ Current research primarily covers the modification of existing fluids and, to a much smaller degree, the screening approach. Major efforts are being expended on the inorganic fluids of ammonia and water and on fluorinated refrigerants, methyl alcohol, and methylamine of the organic fluid family.

As early as 1971, the following absorbent-refrigerant pairs were being investigated by the Russians: Freon-22 with dimethyl ether of tetraethylene glycol, methylamine with water, and ethylamine and water.⁴² The operating conditions used in the pilot refrigerator built for evaluation purposes were $T_{\text{evap}} = -10^{\circ}\text{C}$, $T_{\text{condens}} = 35^{\circ}\text{C}$, and $T_{\text{gener}} = 120^{\circ}\text{C}$. The Russian researchers concluded that the F-22-DMETG fluid pair was the most suitable mixture.

In 1983 scientists in India reported investigations of a large number of promising binary mixtures.⁴³ They considered ammonia, sulphur dioxide, and fluorocarbons as refrigerants in combination with numerous absorbents. A comparison of the working fluids was made for the following refrigerator conditions: $T_{\text{evap}} = 5^{\circ}\text{C}$, $T_{\text{condens}} = 35^{\circ}\text{C}$, and $70^{\circ}\text{C} < T_{\text{gener}} < 125^{\circ}\text{C}$. None of these binary mixtures is appropriate for the application proposed here. Another investigation reported by the Japanese in 1983 considered 70 fluorocarbons and over 150 organic compounds as absorbents.⁴⁴ From this study, the best absorbent-refrigerant pair was determined to be R-22-DEGME, which is Freon-22 and bis(2-methoxyethyl) ether as an absorbent. This report gives plots of the vapor pressure, specific heat capacity, and heat of mixing measured experimentally. The upper limit temperature for this mixture is 200°C, which is still too low to be useful for this application.

1. Cycle Operation. None of the research articles cited proposes a candidate fluid for an absorption refrigerator operating between 150°C and 320°C. Even if a mixture could be found, the maximum theoretical COP would be

$$\text{COP} = \frac{423}{593-423} \cdot \frac{623-593}{623} = 0.12 \quad , \quad (77)$$

which is too small to be feasible.

Closer examination of the temperatures at which heat is added and rejected in this cycle shows that heat must be rejected to the wellbore at 320°C from both the absorber and the condenser. Then the heat added in the generator would require using electrical energy in a heating coil or resistance heater to evaporate the refrigerant from the strong solution, rather than using waste heat.

2. Conclusions. To reject the quantity of heat Q_a at the low temperature in the absorber, an additional quantity of heat must be added to raise the fluid temperature high enough to allow heat to be rejected to the hot wellbore. The heat added in the generator would also require using additional electrical energy in a heating coil or resistance heater (in addition to using heat from the wellbore) to evaporate the refrigerant from the strong solution. For all the reasons stated, the absorption refrigeration system is no longer being considered for active cooling of downhole instruments.

SECTION II

IX. THERMOELECTRIC REFRIGERATION

A. History

Thermoelectric effects were first noticed in the nineteenth century, but did not become useful until the technology revolution created by semiconductor usage during the 1950s. In 1921, Thomas Seebeck found that, by heating the junction between two metals, he could produce an electromotive force. Then, in 1934, Jean Peltier discovered that, by passing an electric current through the junction between two dissimilar metals, he could produce either a heating or a cooling effect, depending upon the direction of the current. Later, Lord Kelvin formulated the connection between the effects based entirely upon thermodynamics and concluded that there must be a third thermoelectric effect. He derived the relationship that gives the lateral heating or cooling of a single conductor through which heat and electric current flow.⁴⁵ It was not until the early twentieth century that all of the effects were formulated into a basic theory for thermoelectric generators and refrigerators. In 1909 and 1911, Altenkirk published work that identified the material properties necessary for the production of a practical thermoelectric device. Both a refrigerator and a generator require high Seebeck coefficients, high electrical conductivities to minimize the Joule heating, and low thermal conductivities to minimize the heating caused by pure conduction. This group of parameters is combined into a variable called the figure-of-merit and is given by the equation

$$F = (\gamma^2)/RK \quad . \quad \quad \quad ^{46} \quad \quad \quad (78)$$

B. Theory

Figure 29 shows a schematic of a thermoelectric refrigerator. The semiconductor branches are connected electrically in series by a link assumed to have no electrical resistance at the heat source and to a voltage source at the heat sink. The branches are thermally in parallel between the heat source at T_c and the heat sink at T_h , which are the actual junction temperatures. There is no lateral heat transfer in the branches of the

Fig. 29. Schematic of a thermo-electric refrigerator.

device; it is assumed to be well-insulated. For preliminary analysis, the geometry of the branches is assumed to be constant cross section but not necessarily of the same length. It is lastly assumed that there is no thermal contact resistance between the reservoir and the connecting bus bar, which is probably the weakest of the above assumptions. A heat balance on the refrigerator, shown in Fig. 29 at the cold reservoir, involves heat from the Peltier effect, Joule heating, and heat transferred by pure conduction. The Peltier heating is given by

$$Q_{p1} = -\gamma_1 IT_c \text{ and } Q_{p2} = \gamma_2 IT_c . \quad (79)$$

The Joule heating is given by

$$Q_{j1} = + I^2 \ell_1 / (2A_1 \sigma_1) \text{ and } Q_{j2} = + I^2 \ell_2 / (2A_2 \sigma_2) , \quad (80)$$

and, finally, the conduction heat transfer is expressed as

$$Q_1 = -k_1 A_1 (T_h - T_c) / l_1 \text{ and } Q_2 = -k_2 A_2 (T_h - T_c) / l_2 . \quad (81)$$

Summing all the heat flows at the heat source gives the cooling power as⁴⁶

$$Q_{cool} = IT_c (\gamma_2 - \gamma_1) - \frac{I^2}{2} \left(\frac{\ell_1}{A_1 \sigma_1} + \frac{\ell_2}{A_2 \sigma_2} \right) - (T_h - T_c) \left(\frac{k_1 A_1}{\ell_1} + \frac{k_2 A_2}{\ell_2} \right) . \quad (82)$$

Q_{cool} = Peltier - Joule - thermal conduction for

$$K = k_1 A_1 / \ell_1 + k_2 A_2 / \ell_2 \text{ and } R = \ell_1 / A_1 \sigma_1 + \ell_2 / A_2 \sigma_2 , \quad (83)$$

leaving Q_{cool} as

$$Q_{cool} = IT_c (\gamma_2 - \gamma_1) - I^2 R / 2 - K \Delta T . \quad (84)$$

The minimum voltage required to run a refrigerator is the voltage necessary to overcome the IR drop plus the voltage necessary to overcome the Seebeck emf or

$$V = (\gamma_2 - \gamma_1) \Delta T + IR, \quad (85)$$

so the power input is

$$P = IV = (\gamma_2 - \gamma_1) I \Delta T + I^2 R. \quad (86)$$

Refrigerator efficiencies are given by the COP, which is the ratio of the heat extracted from the heat source and the power input to the device, or⁴⁶

$$\text{COP} = \frac{IT_c(\gamma_2 - \gamma_1) - I^2 R/2 - K \Delta T}{(\gamma_2 - \gamma_1) I \Delta T + I^2 R}. \quad (87)$$

The total Seebeck coefficient is defined as the absolute value

$$\gamma = |\gamma_1| + |\gamma_2|. \quad (88)$$

There are several ways to optimize the design of a single-stage thermoelectric refrigerator. The simplest involves optimizing the geometry. This suggests that the product of the total branch conductance and total branch resistance must be a minimum:

$$RK_{\min} = \left[\left(\frac{k_1}{\sigma_1} \right)^{1/2} + \left(\frac{k_2}{\sigma_2} \right)^{1/2} \right]^2 \quad (89)$$

Minimizing the RK product leads to a maximum figure-of-merit given by

$$F_{\max} = \gamma^2 / RK_{\min}. \quad (90)$$

Then the maximum COP for the given temperature difference and optimum geometry is⁴⁶

$$\text{COP}_{\text{geom}} = \frac{T_c}{\Delta T} \left[\frac{(1 + FT_m)^{1/2} - T_H/T_c}{(1 + FT_m)^{1/2} + 1} \right], \quad (91)$$

and the required input current is

$$I_{\text{geom}} = \frac{\gamma \Delta T}{R \left[(1 + FT_m)^{1/2} - 1 \right]} . \quad (92)$$

The second optimization of a single-stage refrigerator design involves maximizing the heat extracted from the heat source. In this case, the COP becomes⁴⁶

$$\text{COP}_q = \frac{1/2 FT_c^2 - \Delta T}{FT_H T_c} , \quad (93)$$

and the required input current is

$$I_q = \left| \gamma \right| \frac{T_c}{R} . \quad (94)$$

The last and limiting optimization is the determination of the maximum delta T achievable without requiring heat removal from the heat source at T_c . In this case, the cooling power and the COP are both zero, leaving:⁴⁵

$$(T_H - T_c)_{\text{max}} = 1/2 FT_c^2 . \quad (95)$$

C. Single-Stage Thermoelectric Refrigerator

A preliminary analysis of a single-stage thermoelectric generator is made assuming that the thermal and electrical properties are temperature - independent and that the contact resistances are negligible. These assumptions are quite good for a thermocouple. The weakest assumption as applied to a refrigerator is for the thermal contact resistance at the hot and cold junctions.

Three semiconductor material pairs were chosen based on a plot of the dimensionless figure-of-merit as a function of the absolute temperature as

shown in Fig. 30.⁴⁶ The material properties are listed in Table XXI. The Pb-Te material pair doped with sodium has a dimensionless figure-of-merit that increases with increasing temperature from 97°C to 327°C. The plot for the Bi₂Te₃ material pair shows a maximum for both N and P materials near 127°C. The PbTe and GeTe material pair shows both trends with the n material having an increasing figure-of-merit and the P material reaching a maximum at 427°C.

Table XXII lists the parameters used in numerical hand calculations made for the design of a single-stage thermoelectric refrigerator using the above materials. The cold face must be maintained at 150°C and the hot face at 320°C. At this given temperature difference, the heat pumping rate and the external/internal load resistances are optimized. The average element temperature is 235°C. The lower part of Table XXII lists the required input current and the net cooling power for refrigerators designed to maximize the COP and the cooling power. The last line of Table XXII gives the optimized maximum T achievable, which is smaller than the stated conditions. Therefore, the calculated cooling power is negative and the current required is greater than can be supplied over the existing cable. It was concluded from these calculations that none of the material pairs designed as a single-stage thermoelectric refrigerator can function to provide any net cooling at the stated hot and cold reservoir temperatures.

D. Multiple-Stage Thermoelectric Refrigerator

Multiple-stage thermoelectric refrigerators are designed as sets of P-N material pairs connected electrically in series and thermally in parallel between a hot and cold reservoir. Multiple-stage refrigerators rarely result in efficiency gains, but they do improve the optimum load resistance and the input voltage.⁴⁷

Because multiple stages are electrically in series, the current calculated for a single-stage refrigerator must pass through each stage and is the same. The input voltage increases because of the increased series resistance and Seebeck emf of each additional stage and is

$$V = N \cdot (\gamma_2 - \gamma_1) \Delta T + N \cdot IR \quad . \quad (96)$$

Fig. 30. Dimensionless figure of merit plotted vs temperature.

TABLE XXI

SEMICONDUCTOR MATERIAL PROPERTIES AT $\bar{T} = 508^\circ\text{K}$

Material	Type N/P	α (nV/K)	$\rho \times 10^3$ ohm-cm	$k \times 10^3$ (W/cm-K)	$F \times 10^3$ (1/K)
$\text{Bi}_2\text{Te}_3\text{-Sb}_2\text{Te}_3$	P	166	2.02	0.969	1.39
$\text{Bi}_2\text{Te}_3\text{-Bi}_2\text{Se}_3$	N	-186	1.58	1.183	1.84
GeTe-AgSbTe	P	240	4.52	0.719	1.77
SnTe-PbTe	N	-78	0.60	1.748	0.58
$\text{PbTe-1\%Na}$	P	191	1.77	1.728	1.25
$\text{PbTe-0.055\% PbI}_2$	N	-166	0.92	2.223	1.378

^aRef. 47.

TABLE XXII
SINGLE-STAGE THERMOELECTRIC REFRIGERATORS

<u>Parameter</u>	<u>BiTe</u>	<u>AgSbTe</u>	<u>PbTe</u>
γ_n/γ_p	0.798	0.234	0.636
$\alpha(\mu\text{V/K})$	351	330	357
$F_{\text{max}} (1/\text{K})$	1.603×10^{-3}	1.256×10^{-3}	1.26×10^{-3}
$RK_{\text{min}} (\text{V/K})$	7.668×10^{-5}	8.05×10^{-5}	10.11×10^{-5}
$R (\text{ohms})$	4.0×10^{-3}	7.08×10^{-3}	3.23×10^{-3}
$K (\text{W/K})$	1.917×10^{-2}	1.128×10^{-2}	3.14×10^{-2}
m^1_{opt}	1.347	1.279	1.28

Power and Current: Results

$I_{\text{geom}} (\text{amps})$	43	27.3	67.06
$Q_{\text{geom}} (\text{W})$	-0.572	-0.884	-2.473
$I_{\text{qmax}} (\text{amps})$	37.1	11.9	46.7
$Q_{\text{qmax}} (\text{W})$	-0.503	-0.317	-1.811
$\Delta T_{\text{max}} (\text{K})$	143.7	121	112.8

The power input required is then given by

$$P = N\gamma I \Delta T + NI^2 R = N \cdot IV \quad . \quad (97)$$

The net heat removed is obtained by summing the heat removed for each stage and is given by

$$Q_{\text{cool}}^{\text{tot}} = NIT_c (\gamma_2 - \gamma_1) - \frac{NI^2 R}{2} - NK \cdot \Delta T = N \cdot Q_{\text{cool}} \quad . \quad (98)$$

The COP for a multiple-stage refrigerator is given by the quotient of the total heat removed at the cold reservoir and the total input power or

$$\text{COP} = \frac{Q_{\text{cool}}^{\text{tot}}}{P} = \frac{N \cdot Q_{\text{cool}}}{N \cdot IV} = \frac{Q_{\text{cool}}}{IV} \quad . \quad (99)$$

Thus, the COP is independent of the number of stages. It was concluded from the above discussion and the results of the single-stage refrigerator calculations that none of the material pair candidates could function to provide net cooling between the specified reservoir temperatures even when designed as multistage refrigerators.

E. Cascaded Thermoelectric Refrigerator

Examination of the last line of data in Table XXII shows the maximum temperature difference achievable using a single-stage refrigerator. All the values are less than the required 170°C temperature difference. Therefore, the calculations for a refrigerator arranged in cascaded stages will be made in an effort to achieve the desired temperature difference.⁴⁸

A set of hand calculations to size a two-stage cascaded thermoelectric refrigerator was completed using two combinations of the material pairs listed in Table XXIII. Both refrigerators were sized using the Bi₂Te₃ material pair for the lower-temperature first-stage operating between 150°C and 235°C. The second-stage was sized using the GeTe and SnTe material pair in the first case and the PbTe pair in the second case. The second stage was assumed to operate between 235°C and 320°C.

In this refrigerator design, shown schematically in Fig. 31, the N and P materials in each stage are electrically in series and thermally in parallel between plates at fixed temperatures. The first stage is placed between the cold reservoir, where it must absorb the heat load, and the intermediate temperature plate at 235°C. Then by the first law, the heat rejected to the intermediate plate is the sum of the cooling load plus the power input to the first stage or

$$\begin{aligned} q_1 &= \text{cooling load, and} \\ q_2 &= q_1 + IR_1 . \end{aligned} \tag{100}$$

The second stage must absorb q_2 and then reject q_2 , in addition to the power added to the second stage or q_3 , as in

$$q_3 = q_2 + IR_2 . \tag{101}$$

Each stage is designed in the same fashion as the single-stage refrigerators. The COP of each stage is given by

$$\text{COP} = \frac{q_1}{P_i} , \tag{102}$$

and the total COP is^{48,49}

$$\text{COP}_{\text{tot}} = \frac{q_1}{\Sigma P_i} . \tag{103}$$

Tables XXIV and XXV list the results of the hand calculations for the first- and second-case refrigerators, respectively. These designs were done to optimize the geometry and load resistance to maximize the COP. Table XXVI lists the same parameters for the second-case refrigerator designed to maximize the cooling power. In all cases the required input power is too large by factors of 11X, 6X, and 5X. The overall COPs are 0.0036, 0.071,

Fig. 31. Two-stage cascaded refrigerator.

TABLE XXIII

SEMICONDUCTOR MATERIAL PROPERTIES -- CASCADED DESIGN

Material	Type N/P	α (hV/K)	$\rho \times 10^3$ ohm-cm	$k \times 10^3$ (W/cm-K)	$F \times 10^3$ (1/K)	
Bi ₂ Te ₃ -Sb ₂ Te ₃	P	192.7	1.92	10.07	1.92	at $\bar{T} = 193^\circ\text{C}$
Bi ₂ Te ₃ -Bi ₂ Se ₃	N	-191	1.455	12.54	2	
GeTe-AgSbTe	P	240	4.42	7.08	1.84	at $\bar{T} = 283^\circ\text{C}$
SnTe-PbTe	N	- 85.5	0.73	13.35	0.75	
PbTe-1%Na	P	233	2.5	17	1.277	at $\bar{T} = 283^\circ\text{C}$
PbTe-0.055%PbI ₂	N	-180	1.25	21	1.234	

TABLE XXIV

CASCADED THERMOELECTRIC REFRIGERATOR CASE 1

Parameter	First Stage Bi ₂ Te ₃ Pair	Second Stage AgSbTe Pair
γ_n/γ_p	0.608	0.0876
$\alpha(\eta V/K)$	383.7	325.5
$F_{max} (1/K)$	1.959×10^{-3}	1.395×10^{-3}
$RK_{min} (V/K)$	7.514×10^{-5}	7.596×10^{-5}
R (ohms)	4.313×10^{-3}	12.75×10^{-3}
K (W/K)	17.69×10^{-3}	8.249×10^{-3}
m^1_{opt}	1.383	1.332
I (amps)	19.74	19.74
QC_1 (W)	0.86	0.0788
N	10	404
V	0.1177	0.279
P_1	23.24	222.8
COP_1	0.3442	0.0143
COP_{TOT}	0.0036	-----

TABLE XXV

CASCADED THERMOELECTRIC REFRIGERATOR -- CASE 2

Parameter	First Stage Bi ₂ Te ₃	Second Stage PbTe
γ_n/γ_p	0.608	0.636
$\alpha(\eta V/K)$	383.7	413
$F_{max} (1/K)$	1.959×10^{-3}	1.259×10^{-3}
$RK_{min} (V/K)$	7.514×10^{-5}	13.55×10^{-5}
R (ohms)	4.313×10^{-3}	4.465×10^{-3}
K (W/°K)	17.69×10^{-3}	30.356×10^{-3}
m^1_{opt}	1.383	1.304
I (amps)	19.74	19.74
QC_1 (W)	0.86	0.692
N	10	46
V	0.1177	0.1232
P_1	23.24	111.9
COP_1	0.3442	0.2845,
COP_{TOT}	0.071	-----

TABLE XXVI

CASCADED THERMOELECTRIC REFRIGERATOR -- CASE 3

Parameter	First Stage Bi Te	Second Stage PbTe
γ_n/γ_p	0.825	0.650
$\alpha(\eta V/K)$	383.7	413
$F_{max} (1/K)$	1.983×10^{-3}	1.259×10^{-3}
$RK_{min} (V/K)$	7.425×10^{-5}	13.55×10^{-5}
R (ohms)	3.683×10^{-3}	4.423×10^{-3}
K (W/°K)	20.41×10^{-3}	30.65×10^{-3}
m^1_{opt}	1.387	1.304
I (amps)	22.89	22.89
QC_1 (W)	1.015	1.0384
N	8	29
V	0.1169	0.1363
P_1	21.41	90.50
COP_1	0.3736	0.325,
COP_{TOT}	0.088	-----

0.088 for each case, respectively. It was shown in Section I that the COP must be at least 15% of the Carnot COP of 2.488 to be feasible with the present downhole systems.

It has been concluded from these calculations that none of the cascaded refrigerator designs can provide the required cooling power between the stated reservoir temperatures at the required maximum input power or COP.

F. Segmented Thermoelectric Refrigerator

A segmented thermoelectric refrigerator is shown schematically in Fig. 32. Each leg of the refrigerator is composed of segments of different materials. Each material segment is chosen to operate across its most efficient temperature range. The material segments are electrically in series and thermally in series between reservoirs. Each leg must be designed such that there is no net heat flowing into any of the junctions between segments. The following condition must be satisfied at each P material boundary where $J_p = I/A_p$:

$$K_{p,i} \left(\Delta T_{p,i} / L_{p,i} \right) + 1/2 \rho_{p,i} J_p^2 L_{p,i} - K_{p,i+1} \left(\Delta T_{p,i+1} / L_{p,i+1} \right) + 1/2 \rho_{p,i+1} J_p^2 L_{p,i+1} - \left(\gamma_{p,i+1} - \gamma_{p,i} \right) T_{p,i} J_p = 0 \quad , \quad (104)$$

and a similar equation for the n materials with $J = -I/A_n$.⁴⁷

The design of a segmented device has fewer adjustable parameters than a cascaded device because of the added constraints at each material interface. Because of this, the efficiency of a segmented device is always less than or equal to the efficiency of a cascaded device operating between the same temperature ranges using the same materials.^{49,50}

Because the cascaded refrigerator did not prove feasible, it is concluded that a segmented device would not be feasible and will not be considered further.

G. Summary

A series of design calculations has been completed to size a thermoelectric refrigerator for use in cooling downhole instrumentation. The cooling load is stated as 8 W, to be removed at 150°C and then

Fig. 32. Segmented arm refrigerator.

rejected at 320°C. Design investigations were made for the following refrigerator configurations:

- a) single-stage - three material pairs,
- b) multiple-stage,
- c) two-stage cascaded - three cases, and
- d) single-stage segmented.

The results for the single-stage design shows a negative cooling power for all three material pairs, and the devices could not function as a refrigerator under the stated conditions. The multiple-stage design is also not feasible, because it is merely a series composite of many single-stage refrigerators. The results for the two-stage cascaded design show that all three cases can function as a refrigerator with the design optimized for maximum cooling power being the best solution. Even this design is not feasible because it requires at least five times more power input than is available with the present system. Because single-stage segmented devices are inherently less efficient than the corresponding cascaded designs, they were also not considered feasible.

It was concluded from these calculations that a thermoelectric refrigerator cannot function under the constraints imposed on this design and will not be considered further.

X. MAGNETOCALORIC REFRIGERATION

A. Background

Energy conversion and refrigeration can be accomplished using the magnetocaloric effect. Adiabatic magnetization and demagnetization of a ferromagnetic substance near its Curie point produces a cyclic, repeatable temperature change. The Curie point is the temperature above which ferromagnetic materials abruptly lose their internal magnetization.⁵¹

The use of this phenomenon in an energy conversion device was proposed and patents were applied for by Edison in 1887 and by Tesla in 1890. It was not until L. Brillouin and H. P. Iskenderian wrote a paper in 1948 that a serious attempt was made to write out the magnetocaloric theory to calculate the power output or the thermodynamic efficiency of a generator.⁵²

Practical application of magnetocaloric devices is restricted by several factors. Ferromagnetic materials typically have very high Curie point temperatures: nickel at 354°C, iron at 771°C, and cobalt at 1115°C.⁵¹ Because most materials experience a degradation in magnetic properties at high temperatures, this poses a distinct disadvantage because the ferromagnet and other parts of the magnetic circuit must be in close contact. But the most severe disadvantage is the fact that the transition between ferromagnetic and paramagnetic behavior is so abrupt that the thermodynamic efficiency is very low because of the small temperature differences involved in the process.

B. Thermodynamic Cycle

A thermodynamic cycle must be experienced by the ferromagnetic substance to use the magnetocaloric effect in a refrigerator. The Carnot cycle for a ferromagnetic is illustrated in Fig. 33 and consists of two isothermal and two isentropic steps that occur with the ferromagnetic substance near its Curie point.

Isothermal magnetization occurs between States 4-3, while the heat of magnetization is being rejected to the hot bath to maintain a constant temperature, T₂. A partial demagnetization occurs between States 3-2 that cools the material down to the cold bath temperature, T₁. Then the material is demagnetized to zero field between States 2-1, while heat is being drawn from the cold bath to maintain constant temperature, T₁. The last step between States 1-4 is a partial magnetization, which heats the material back up to its starting hot bath temperature, T₂. Figure 33 illustrates the T-S diagram with constant field lines and Fig. 34 shows a T-i diagram for the same cycle.

C. Theory

The energy stored in this magnetocaloric system is composed of thermal and magnetic contributions. From the first law, the stored energy increments are:

$$dU(S, \psi) = dQ + dW = id\psi \quad .^{51} \quad (105)$$

Fig. 33. Magneto-caloric Carnot cycle temperature-entropy diagram.⁵⁵

Fig. 34. Temperature current diagram.⁵¹

Because the temperature and the current in a device are readily measurable, the incremental energy equation is transformed into the following form:

$$dU(T,i) = T \left(\frac{\delta S}{\delta T_i} dT + \frac{\delta S}{\delta i_T} di \right) + i \left(\frac{\delta \psi}{\delta T_i} dT + \frac{\delta \psi}{\delta i_T} di \right) = \left(C^i + i\psi_T \right) dT + \left(C^T + iy_i \right) di \quad (106)$$

Then the thermal and magnetic contributions are separated with

$$dW_Q = TdS = C^i dT + C^T di \quad (107)$$

being the general expression for an increment in the thermal energy and

$$dW_\psi = id\psi = i\psi_T dT + iL di, \text{ for } i = L(T_i i) \quad (108)$$

being the general expression for an increment in the magnetic field energy.

For the ferromagnetic material the expressions are

$$dW_Q = C(T)dT - TL_K idi \quad (109)$$

$$dW_\psi = iL_K dT + iL_K(\theta - T)di \quad .^{51} \quad (110)$$

An energy balance on the cycle operating at steady state requires that the net thermal energy input be equal to the net magnetic field energy output as

$$dW_{Q_{3-4}} + dW_{Q_{1-2}} = dW_{\psi_{net}} \quad (111)$$

The thermal energy exchange evaluated along the process between State Points 1-2 and 3-4 is

$$dW_Q = C(T)dT - TL_K idi \quad (112)$$

where the incremental current term is the only contribution, or

$$W_{Q_{1-2}} = -T_1 L_K \int_{i_1}^{i_2} i di = T_1 L_K \frac{i_2^2}{2} \quad (113)$$

is the heat input and

$$W_{Q_{3-4}} = -T_2 L_K \int_{i_3}^{i_4} i di = \frac{-T_2 L_K}{2} (i_4^2 - i_3^2) = T_2 L_K \frac{i_3^2}{2} \quad (114)$$

is the heat rejected. So the net thermal energy is

$$dW_{Q_{net}} = \frac{L_K i_2^2}{2} (T_2 - T_1) , \quad (115)$$

which is also the net magnetic field energy output. The thermodynamic efficiency is given by

$$n = \frac{W_{out}}{Q_{in}} = \frac{L_K i_2^2}{2} (T_2 - T_1) \cdot \frac{2}{L_K i_2^2} \cdot \frac{1}{T_1} = \frac{T_2 - T_1}{T_1} , \quad (116)$$

or the same as the Carnot efficiency, as expected.

A calculation of the upper limit for the efficiency was made that includes electrical, magnetic, and thermal energies. The resulting expression is a ratio of the magnetizing field to the Weiss field as

$$E < \frac{\pi(HI/2)}{NI^2/2} = \frac{\pi H}{NI} \cdot \quad (117)$$

Assuming the device is built using iron for which

$$H = 10 \text{ to } 100, \text{ and} \quad (118)$$

$$NI^2 \approx 10^7 ,$$

then the efficiency is

$$E_{\min} = \frac{\pi \times 10}{10^7} = \pi \times 10^{-6}, E_{\max} = \frac{\pi \times 100}{10^7} = \pi \times 10^{-5}, \text{ or} \quad (119)$$

$$10^{-4}\% < E < 10^{-3}\% ,$$

which is very small.

A similar calculation was made assuming use of gadolinium as a shunt material and Alnico XII as the permanent magnet, with the resulting efficiency of

$$E = 0.57\% \quad 54 \quad (120)$$

All of the above efficiencies are very low because of the abruptness, or the very small T , over which the magnetic behavior changes at the Curie point.

If this device is operated in reverse as a refrigerator, the cycle heat balance is

$$W_{\psi} = Q_{\text{reject}} - Q_{\text{refrig}} \quad (121)$$

Calculation of the required work input is made by using the net thermal energy exchange terms. The thermal energy terms for heat absorption and heat rejection are, respectively

$$W_{Q_{2-1}} = T_1 L_K \frac{i^2}{2}, \text{ and} \quad (122)$$

$$W_{Q_{4-3}} = -T_2 L_K \frac{i^2}{2},$$

so that the net thermal energy is

$$W_{Q_{\text{net}}} = -L_K \frac{i^2}{2} (T_2 - T_1), \quad (123)$$

which is also the required magnetic field energy input.

The COP is evaluated as

$$\text{COP} = \frac{Q_{\text{refrig}}}{W_{\text{in}}} = T_1 L_K \frac{i^2}{2} \cdot \frac{2}{L_K i^2} \cdot \frac{1}{T_2 - T_1} = \frac{T_1}{T_2 - T_1}, \quad (124)$$

which is the same as the Carnot COP, as expected. In this application, the COPs are quite high because of the small temperature change. Also, the COP increases with increasing Curie point temperature. Operating refrigeration devices using the magnetocaloric effect have been reported with COPs as large as 80% of Carnot.⁵⁵ The major disadvantage of such a refrigerator is the small temperature difference between hot and cold reservoirs.

D. System Components

For the refrigerator to operate, a heat transfer fluid must exchange heat with the ferromagnetic material to complete the $W_{Q_{2-1}}$ heat absorption process and the $W_{Q_{4-3}}$ heat rejection processes. Thus, a magnetocaloric refrigerator system must include more elements than just a magnet and an induction coil. The components of the ferromagnetic circuit used for this study are a permanent magnet, an induction coil, a ferromagnetic shunt material, a heat transfer fluid, and a minimum of two external heat exchangers, one fluid drive pump, and a motor to move the shunt material in and out of the magnetic field. Figure 35 illustrates a schematic of a rotational-cycle magnetic refrigerator.⁵⁶

Components for the system (shown in Fig. 33) depend upon the choice of the heat rejection temperature. A series of ferromagnetic shunt materials must be found with Curie points and adiabatic temperature change that span the temperature range of the refrigeration process under study. Then, the magnetic properties must be known as a function of temperature and magnetic field intensity. Relevant properties are the permeability, μ , the susceptibility, χ , and the specific heat at constant field intensity, C^H . Given this information, the temperature change produced by adiabatic magnetization is given by

$$\Delta T = \frac{-T}{C^H} \frac{\gamma^M}{\gamma^T_H} \Delta H, \quad 57 \quad (125)$$

where M = internal magnetization moment.

The heat absorbed by the ferromagnetic material subjected to cyclic magnetizations is given by

$$\dot{Q}_{abs} = V \rho f \bar{T}_c \Delta S D, \quad 55 \quad (126)$$

where V = volume of the ferromagnet,

ρ = density of the ferromagnet,

D = frequency of the magnetizations,

$\bar{T}_c$ = refrigeration load temperature,

ΔS = entropy change caused by the magnetization, and

f = fraction of ferromagnet action in process.

For a specified refrigeration load and known $\bar{T}_c$ and ΔS , the mass of the ferromagnet can be determined. The size of the permanent magnet depends upon the properties of the ferromagnet, because the B field produced by the inductor and the core must be very close to the saturation field of the ferromagnet.

E. Component Selection Criteria

The basic mechanical and thermodynamic processes recommended are the Carnot-cycle wheel device or the Carnot-cycle reciprocating refrigerator. Both are relatively simple in concept, and there are prototypes presently operating at cryogenic temperatures.^{55,56}

The criteria for selection of a magnetic refrigerant are outlined by Barclay in great detail for low-temperature applications.⁵⁶ The same general criteria apply for higher temperatures with the two most important considerations being that the material must have a large value of the effective Bohr magneton number and must have a Curie point in the range above 27°C. The ferromagnetic metals and their compounds with the rare earth ions are thought to be good working materials.⁵⁸

Fig. 35. Rotational Carnot cycle magneto-caloric refrigerator.

Fig. 36. Candidate magnetic refrigerant T-S diagram.

Selection of a good heat transfer fluid requires that it be conducive to providing a good heat transfer coefficient, so it should have a high specific heat and density and moderate conductivity. A heat exchange geometry must then be chosen that maximizes the heat transfer processes with a minimum frictional pressure loss and longitudinal heat conduction. The three geometries that can provide these requirements are 1) flow through a circular tube bank, 2) flow through parallel flat plates, and 3) flow through a fine-grained porous bed.

F. Conceptual Design

Only four refrigerants were found with a Curie point lying between 77°C and 327°C.⁵⁹ The data available for refrigerants in the temperature range above 27°C are almost nonexistent because the primary interest in magnetocaloric refrigeration has been for cryogenic temperatures. The selected refrigerants, their Curie points, the temperature change induced by an adiabatic demagnetization, and their isothermal heat pumping capacity are listed in Table XXVII.

A temperature-entropy plot, Fig. 36, of the candidate materials shows achievable refrigeration cycles and areas in which refrigerants are missing. Refrigerants are missing in the ranges between 150°C and 210°C, between 220°C and 296°C, and between 306°C and 327°C. Osterreicher predicted that compounds of the intermetallics would work over the range of temperature from 27°C to 327°C.⁶⁰ If this is true, then a refrigerant is available for the complete range of interest, with an average temperature change of 9°C. Assuming no regeneration heat exchange and an average volume entropy change coefficient of $fr=0.62$, the complete system would require 19 separate cooling stages. This would include 20 external heat exchangers, 20 fluid pumps, a minimum of 1 motor to rotate the refrigerants, and very likely several different permanent magnets with a total of 19 sets of induction coils, all of which must be housed in a hot service dewar.

Using Barclay's rules-of-thumb for estimating the volumes of system components as

ferromagnetic material = 1/3 of the housing volume,

housing volume = 1/8 of the field volume,

field volume = 1/5 of the magnet volume, and

magnet volume = 1/10 of the overall dewar volume,

the magnetic refrigerant is approximately 1/1200 of the entire system volume.⁵⁶

For this system, the refrigeration load is assumed to be 8 W. Using Eq. 126 for the load and solving for the required volume of the ferromagnetic refrigerant gives

$$V = \dot{Q}_{\text{abs}} / (\rho f T_c \Delta S v) = 1.54 \text{ cm}^3/\text{cycle} \quad . \quad (127)$$

Then allowing for 50% porosity we have

$$V = 3.1 \text{ cm}^3/\text{cycle stage} \quad . \quad (128)$$

For 19 separate cooling stages, the total estimated system refrigerant volume is

$$V_{\text{refrig}} = 58.7 \text{ cm}^3 \quad , \quad (129)$$

and the total system volume is

$$V = 7.042 \times 10^4 \text{ cm}^3 \quad . \quad (130)$$

If the downhole refrigerator must fit inside a 5-1/2-in.-diameter pressure vessel with an inside diameter of at least 4-1/2 in., then the refrigerator is 22-ft long.

G. Preliminary Results

A conceptual design and preliminary analysis have been done to size the components of a magnetocaloric refrigerator operating between 150°C and 320°C and removing an 8-W cooling load. Using state-of-the-art recommendations for choices of the thermodynamic cycle and mechanical arrangement led to a rotating-wheel Carnot cycle without regeneration that requires 19 stages. Only three of those stages have available measured thermodynamic properties. The total volume of the system is $7.04 \times 10^4 \text{ cm}^3$ and would fill a 22-ft-long tube with a 5-1/2-in. diameter. The preliminary results show that the system is too complex and too massive to be of practical use in the proposed application.

TABLE XXVII
CANDIDATE MAGNETOCALORIC REFRIGERANTS

<u>Refrigerant</u>	T_c^c (°C)	ΔT^d (°C)	fr^a	$-T\Delta S_m$ J/cm ³
Gd	25	12.6	1.00	31.38
Sm ₂ Fe ₁₇	95	10.5	0.62	19.45
Fe ₃ C	210	-----	1.05	32.95
Y ₂ Fe ₁₇	296	-----	0.62	19.45
Y ₂ (Co _{0.3} Fe _{0.7}) ₁₇	327	7.5	1.01	31.69

- ^a fr = the volume entropy change coefficient at the Curie Point,
 T_c = normalized to gadolinium.
^b $-T\Delta S_m$ = the isothermal heat pumping capacity.
^c T_c = the Curie Point temperature.
^d ΔT = the adiabatic cooling response.

XI. ELECTROCALORIC REFRIGERATION

A. Background

Energy conversion between thermal and electrical sources can be accomplished using the electrocaloric effect in much the same manner as the magnetocaloric effect. Polarization and depolarization of an insulating substance near its Curie temperature results in repeatable, cyclic temperature changes. The Curie point is the temperature above which spontaneous polarization disappears,⁶¹ even in the presence of an applied electric field. The use of this phenomenon in an energy conversion device was reported in the 1960s by several authors,^{62,63} but practical application of this effect is limited by many of the same factors limiting the use of the magnetocaloric effect.

B. Electrocaloric Substances

The insulating materials used in capacitors undergo several types of polarizations. Polarization occurs in all forms of dielectric insulators and is not accompanied by a loss of energy.⁶⁴ Insulating materials are

divided into several classes as follows: a) dielectrics with polarization independent of temperature, b) paraelectrics with polarization temperature-dependent, and c) ferroelectrics that have a spontaneous polarization below the Curie point and have no linear correlation between the polarization and the electric field.⁶⁵ The insulating material used in an electrocaloric converter is a ferroelectric substance. Ferroelectric materials are a subset of pyroelectric materials that undergo a change in their permanent polarization field upon a change in the temperature. Every pyroelectric substance is also piezoelectric, but not every piezoelectric substance is pyroelectric. Piezoelectric materials undergo a change in the permanent polarization field upon a change in the stress state (or the state of strain). Ferroelectrics are further broken down by classes according to their spontaneous polarization along one axis or along several axes⁶⁵ as well as into classes according to whether the ferroelectric transition is first or second order.⁶⁶

The converter discussed below (Fig. 37) assumes use of a pyroelectric ferroelectric crystal that undergoes a first-order transition at the Curie point.⁶⁷ The Carnot cycle is used to describe the electrocaloric conversion process. This cycle is used on the assumption that the incremental energies involved in the process are primarily thermal and electrostatic and that the strain energy is negligible. If the strain energy were to be included in the formulation, the cycle would be based on a Stirling cycle, with an efficiency the same as that for a Carnot cycle between the same temperatures.

C. Thermodynamic Cycle

A thermodynamic cycle must be experienced by an electrocaloric substance to use the effect in an engine or a refrigerator. The equivalent Carnot cycle for an electrocaloric engine is illustrated in Fig. 38 and consists of two isentropic processes and two isothermal charging and discharging processes that occur near and above the Curie point.⁶⁷ Figure 39 illustrates the electrocaloric cycle on charge and voltage coordinates.

Isothermal polarization, or charging of the capacitor, occurs between States 1 and 2 at the cold reservoir temperature T_c , which is at or slightly

Fig. 37. Electrocaloric energy converter.

Fig. 38. Ideal Stirling cycle for an electrocaloric refrigerator.

above the Curie point. The temperature of the capacitor is then increased from T_c to T_h by the heat supplied at State 2. The relationship between charge, capacitance, and voltage is given by⁶⁸

$$Q = CV , \quad (131)$$

where Q = charge,

C = capacitance, and

V = voltage.

The dielectric constant and the capacitance decrease with increasing temperature, as shown in Fig. 40, at or above the Curie point, in a manner described by the Curie-Weiss law.⁶⁹ Because the charge on the capacitor is the same between Points 2 and 3, the decrease in capacitance must be compensated by an increase in the voltage, which in turn causes an increase in the electrical energy. This increase in energy results in the net output of electrical energy from the cycle.

The capacitor is completely discharged between States 3 and 4, while it is at the hot reservoir temperature T_h . The last step in the cycle involves heat removal at the zero voltage and polarization state to return the electrocaloric material to its initial temperature.

D. Theory

The energy stored in an electrocaloric device, or a capacitor, is composed of thermal and electrostatic contributions. The relation describing these quantities is⁶⁹

$$dU(S,e) = T ds + e dq . \quad (132)$$

Because the temperature and the voltage and the associated changes are readily measurable, the incremental energy equation is transformed to the form

$$dU(T,e) = \left[T \left(\frac{\partial s}{\partial T} \right)_e dT + T \left(\frac{\partial s}{\partial e} \right)_T de \right] + e \left(\frac{\partial q}{\partial T} \right)_e dT + e \left(\frac{\partial q}{\partial e} \right)_T de . \quad (133)$$

Fig. 39. Electrocyclic refrigerator charge-voltage cycle.

Fig. 40. Temperature dependence of the dielectric constant for a ferroelectric material.

This equation is then rewritten in the form of specific energy coefficients and expansion coefficients as

$$dU(T,e) = \left(C^e + eq_T \right) dT + \left(C^T + eq_e \right) de . \quad (134)$$

The thermal energy contribution is given by

$$dW_Q = Tds = C^e dT + C^T de , \quad (135)$$

and the electrical energy contribution is given by

$$dW_e = edq = eq_T dT + eq_e de . \quad (136)$$

During the process from State 1 to State 2, when the capacitor is being charged at the low reservoir temperature, the electrical energy increment is:

$$\Delta W_{e1-2} = Q E_2 / 2 ,^{63} \quad (137)$$

where $Q = C_o V (\theta_o - T)$.

For the temperature to remain constant, the following amount of thermal energy must be removed:

$$\Delta W_{Q1-2} = -1/2 T_c C_o V^2 .^{69} \quad (138)$$

In the next step, the capacitor is heated from State 2 to 3, changing its temperature from T_c to T_h , while keeping the charge constant. There is no electrical energy input, and the thermal energy input during this process is

$$\Delta W_{Q2-3} = C^e dT - T C_o V dV , \quad (139)$$

for which the temperature is obtained from the Curie-Weiss law as

$$T = \theta_o - (Q/C_o V) . \quad (140)$$

This results in the following thermal energy increment⁶⁹

$$\Delta W_{Q2-3} = C^e(T_h - T_c) + Q(V_3 - V_2) - C_o \theta_o (V_3^2 - V_2^2)/2 , \quad (141)$$

which is the heat stored as thermal capacity and the heat required to change the electrical state of the capacitor.

The capacitor is then isothermally discharged in the next step from State 3 to 4, to zero voltage and zero charge. The electrical energy increment is⁶⁹

$$\Delta W_{e2-3} = C_o(\theta_o - T) V dV = -1/2 Q_3 V_3 , \quad (142)$$

and the thermal energy increment is

$$\Delta W_{Q3-4} = -V T C_o dV = T_h C_o V_3^2/2 . \quad (143)$$

The last step in the cycle involves cooling the capacitor from T_h to T_c . This involves a zero increment in electrical energy and the following increment in thermal energy⁶⁹

$$\Delta W_{Q4-1} = C^e dT = C^e(T_h - T_c) . \quad (144)$$

The net thermal energy input over the entire cycle is given by summing heat flow for each process and is

$$dW_{Q_{net}} = 1/2 Q(V_3 - V_2) , \quad (145)$$

which must also be the same as the net electrical output from the cycle, or

$$dW_{e_{net}} = dW_{Q_{net}} . \quad (146)$$

Heat input occurs during processes 2-3 and 3-4 and is given by⁶⁹

$$dW_{Q_{in}} = C^e(T_h - T_c) + 1/2 Q(V_3 - V_2) + 1/2 C_o \theta_o V_2^2 . \quad (147)$$

The thermal efficiency of the cycle is then the ratio of the net electrical work output to the heat input or⁶⁹

$$\eta = W_{out}/Q_{in} = \frac{1/2 Q(V_3 - V_2)}{C^e(T_h - T_c) + 1/2 Q(V_3 - V_2) + 1/2 C_o \theta_o V_2^2} . \quad (148)$$

E. Refrigerants Available

To build an electrocaloric converter or a refrigerator that spans the temperature range considered in this work, a series of ferroelectric materials with Curie points that span the range must be identified. These materials must then have a maximum temperature range that overlaps the adjacent material and have all the material properties available for design purposes. The resistivity, dielectric constant, density, conductivity, and other properties must be known as a function of temperature, particularly near the Curie point. Table XXVIII lists the known ferroelectrics and the material properties that were available after a literature search.⁷⁰ The seven materials that have a Curie temperature that falls inside the range have maximum delta T's of 10° to 30°. This series of materials does not provide an adequate span of either the temperature range or adequate overlap between materials for continuous heat transfer. The materials are plotted in Fig. 41 to illustrate the holes left in the range. The material listed as a solid solution of

$$1/2 (Fe_{1-x}Co_x)_{17} ,^{60} \quad (149)$$

will probably provide the needed span of both the Curie temperatures and the overlaps, but there is no information available from which to do any design calculations. For these reasons, the electrocaloric conversion process is

TABLE XXVIII
FERROELECTRIC MATERIAL PROPERTIES

Material	Curie Point °C	ΔT °C	Dielectric $\times 10^5 \text{ V/cm}$	Specified Heat cal/g-°C	Density g/cm ³	Efficiency %
1) Barium Strontium- Titanate (75-25%) ^a	25	23	.031	0.1	2	--
2) Barium Titanate ^b	107-120	30	1.1	0.1	5.5	0.5
3) BaTiO ₃ ^c	120	10	--	--	--	0.35
KNbO ₃	435	10	--	--	--	0.5
KH ₂ PO ₄	150	10	--	--	--	3.3
Cd ₂ Nb ₂ O ₇	93	10	--	--	--	0.45
4) Lead Titanate ^d PbTiO ₃	490	30	1.0	0.09	7.75	5.6
5) NaNO ₂ ^e	164	5-75	--	0.04	2.16	--
Pb _{1-x} La _x (Zr _{1-y} Ti _y) _{1-x/4} O ₃	100-377	--	--	--	--	--
KNbO ₃	360	--	--	--	4.59	--
6) BaTiO ₃ ; SM-1 ^f	35±10	--	0.03	--	5.5	--
BaTiO ₃ ; SM	125±10	--	0.15	--	5.5	--
7) KNbO ₃ ^g	210&415	--	--	--	--	--

^aRef. 67.

^bRef. 61.

^cRef. 66.

^dRef. 63.

^eRef. 70.

^fRef. 64.

^gRef. 65.

Fig. 41. Candidate electrocaloric refrigerants.

not considered feasible for application in an active cooling system for downhole use.

XII. FUEL CELLS

A. Background

Since ancient times, electrochemical energy was used to gold plate jewelry. In modern times (1799), Alessandro Volta is credited for the concept of the electrochemical series and the first practical fuel cells.⁷¹ Direct conversion of chemical energy to electric current was first accomplished in 1801 when Humphrey Davey built a fuel cell using carbon electrodes and nitric acid as an electrolyte.⁷² Historically, Sir William Grove is credited with developing the first fuel cell using platinum electrodes immersed in sulfuric acid to produce a water forming reaction and, much to his surprise, an electric current.⁷³ Grove was also the first to observe the difficulty in producing high current densities in a fuel cell using gases. Fifty years later, Ludwig Mond and Carl Langer developed improvements to the hydrogen/oxygen fuel cell to produce a 6-amps/ft² output.⁷³ F. T. Bacon is considered the pioneer in modern fuel cell research. In the 1930s he began research to find cheap catalysts for the hydrogen/oxygen fuel cells and, by the early 1950s, had developed a multikilowatt generator⁷³. The development of fuel cells accelerated during the 1950s in answer to the space program's need for an energy source with a high-power output/weight ratio.

Fuel cells can be separated into three general categories: direct, indirect, and regenerative. The direct fuel cells use a fuel and an oxidant to produce electric current and a product that is discarded. In an indirect fuel cell, such as a biochemical cell, a biochemical reaction produces stable products that can be used in an electrochemical fuel cell reaction.⁷³ A regenerative fuel cell uses the reactants to produce electric current and a product that is regenerated into the reactants and then recycled in a closed system. Fuel cells can also be categorized by operating temperature into the following classes: (a) low temperature as $0 < T < 100^{\circ}\text{C}$, (b) medium temperature as $100 < T < 500^{\circ}\text{C}$, (c) high temperature as $500 < T < 1000^{\circ}\text{C}$ and, (d) very high temperature

$T < 1000^{\circ}\text{C}.$ ⁷³ The fuel cells of interest in this study are in the medium-temperature category. Typical examples are hydrogen/oxygen cells, organic/oxygen cells, and ammonia/oxygen cells. The following paragraphs describe the theory and thermodynamics of a medium-temperature direct hydrogen/oxygen fuel cell.

B. System

A fuel cell is a device that converts chemical energy directly into electrical energy without going through a "hot" combustion process. The fuel cell reactions take place at constant temperature and constant pressure, so that the Carnot efficiency limitation does not apply.

Figure 42 shows a schematic of a hydrogen/oxygen fuel cell. The major components are an electrolyte, an anode, a cathode, an external circuit with a load, a fuel, and an oxidizer. The anode is the electrode at which oxidation takes place, and the fuel is separated into positive ions and electrons. The positive ions diffuse into the electrolyte solution and migrate toward the cathode. The electrons pass from the anode, through the external circuit, where they do useful work, and then to the cathode. Reduction reactions occur at the cathode. The positive ions from the electrolyte combine with the electrons and the oxidizer to form a product, in this case, water. For the hydrogen/oxygen fuel cell, the half-reactions and the overall reaction are as follows:

The electrolyte solution completes the circuit by providing a path for the positive ions to cross between electrodes. The fuel cell forces the valence electrons from the fuel to take a path through the external circuit, but they do so only once. The chemical reaction proceeds until the fuel or the oxidizer is exhausted.

The current passing through the external load drops through the entire potential of the fuel cell, thereby giving up almost all of its energy. In contrast, the exhaust gas from a heat engine carries away a large quantity of energy that is unused by the engine. For the efficiency of a Carnot heat engine to approach 100%, it is necessary that the exhaust temperature approach zero or that the exhaust gas give up all its energy to the engine. Because the current flowing in a fuel cell traverses the entire cell potential rather than just a fraction of it, the efficiencies obtainable are very close to 100%.⁷³

C. Theory

Fuel cells produce useful work, reject heat to their surroundings, as well as receive the entering fuel and oxidizer gases and deliver a gas stream of reaction products. The laws of thermodynamics apply to such a device, with the work produced by electrons rather than by a flowing fluid. The first law applied to the schematic shown in Fig. 43 is given as⁷²

$$\bar{dQ} - \bar{dW}_{\text{rev}} = d\bar{U} + \sum dm_e H_e - \sum dm_i H_i \quad (153)$$

If the process is considered reversible, then, by the second law, the entropy change is given as

$$d\bar{S} = \frac{\bar{dQ}}{T} + \sum dm_i S_i - \sum dm_e S_e \quad (154)$$

Solving for the heat transfer from the second law, and substituting it into the first law, the reversible work is given by

$$\bar{dW}_{\text{rev}} = \sum dm_i \left(U_i + PV_i - TS_i \right) - \sum dm_e \left(U_e + PV_e - TS_e \right) - d \left(U - TS \right) \quad (155)$$

The maximum work obtainable from a reversible process is the reversible work minus any work done by the system on its surroundings. If the process is carried out in pressure equilibrium with the surroundings, the work is

Fig. 42. Hydrogen-oxygen fuel cell.⁷³

Fig. 43. Fuel cell schematic.

$$\bar{W}_{\text{surr}} = P_{\text{atm}}(V_2 - V_1) \quad . \quad (156)$$

Combining the work terms gives

$$\bar{W}_{\text{max}} = \bar{W}_{\text{rev}} - \bar{W}_{\text{surr}} \quad . \quad (157)$$

For a closed system or an open system at steady state, $dm_1 = dm_e$ and the maximum useful work is given by⁷²

$$\bar{W}_{\text{max}} = (U_1 + PV_1 - TS_1) - (U_2 + PV_2 - TS_2) \quad . \quad (158)$$

Using the definition of the Gibbs free energy function as

$$G = U + PV - TS \quad 76 \quad (159)$$

gives the maximum useful work obtainable from a fuel cell as

$$\bar{W}_{\text{max}} = G_1 - G_2 = -\Delta G \quad . \quad (160)$$

Assuming that all the useful work is electrical work, which is the current that flows through the external circuit multiplied by the reversible cell voltage,

$$\bar{W}_{\text{max}} = \bar{W}_{\text{elec}} = \eta FV \quad , \quad 72 \quad (161)$$

where η = number of moles of electrons,

F = Faraday, Avogadro's number of electrons per chemical equivalent, and

V = ideal cell voltage.

The total energy change that occurs during the fuel cell reaction is given by the heat of reaction and is defined as

$$\Delta H_{\text{reaction}} = \Sigma \Delta H_{\text{products}} - \Sigma \Delta H_{\text{reactants}} \quad .^{76} \quad (162)$$

Using the Gibbs free energy as defined above, the reversible heat transfer is

$$Q = T\Delta S \quad . \quad (163)$$

Then the total energy change from the fuel cell reaction is given up as reversible work in the form of ΔG and as reversible heat transfer in the form of $T\Delta S$. The intrinsic efficiency of this process is defined in the same manner as for a heat engine as

$$\eta_i = \frac{W_{\text{elec}}}{\Delta H} = \frac{\Delta G}{\Delta H} = \frac{\Delta H - T\Delta S}{\Delta H} = 1 - T \frac{\Delta S}{\Delta H} \quad ,^{72} \quad (164)$$

As long as heat is released and ΔS is negative, the Gibbs free energy is a smaller negative quantity than is the heat of reaction. As the heat release decreases towards zero, which is the limiting case for a reversible reaction, the efficiency approaches 100% in the limit. This expression for efficiency is not restricted by the Carnot temperature difference between hot and cold reservoirs, because the process is isothermal.

The voltage efficiency of a fuel cell is defined as the ratio of the actual cell voltage to the reversible cell potential, or

$$\eta_v = \frac{V}{V_r} \quad .^{73} \quad (165)$$

The faradic efficiency is defined as the ratio of the observed current to the theoretically expected current, or

$$\eta_f = \frac{I}{I_m} \quad .^{73} \quad (166)$$

Therefore, the overall efficiency of a fuel cell is the product of the intrinsic, voltage, and faradic efficiencies as

$$\eta = \eta_i \eta_v \eta_f \quad .^{71,72} \quad (167)$$

In general, the faradic and voltage efficiencies tend toward 100%, and the fuel cell operates at a relatively high efficiency depending upon the intrinsic efficiency. The irreversibilities in the system stem from unwanted reactions at either electrode, impedance to the desired reactions at either electrode, concentration gradients established in the electrolyte, and Joule heating in the electrolyte.

A fuel cell is in itself not a heat engine, but it can be a component in a process that is a heat engine. Regenerative fuel cells differ from the direct fuel cell described above in that the products undergo further reactions to regenerate the original reactants for reuse in the fuel cell. Thus, a regenerative fuel cell is a closed system in which gas streams undergo cyclic thermodynamic processes analogous to those in a Carnot heat engine.

The regenerative fuel cell uses the products as its working fluid and operates in a cycle as follows: (a) fuel and oxidizer react isothermally in the fuel cell to produce electric current and reaction products and release heat at the low temperature, T_1 , (b) the reaction products are heated to a higher temperature by a heat exchanger using an external heat source, (c) the reaction products undergo a chemical reaction to separate the original reactants at the constant temperature, T_2 , and (d) the reactants leaving the separator are cooled by a heat exchanger to the fuel cell operating temperature, T_1 .

The temperature-entropy diagram is shown in Fig. 44. The entire cycle is subject to the limitations of the second law, because it is a heat engine receiving heat from a hot reservoir and rejecting heat to a low-temperature heat sink. Therefore, the Carnot limitation holds for the entire cycle. The work output from the cycle is given by

$$\bar{W} = \Delta G_{41} = -(\Delta H_{41} - T_1 \Delta S_{41}) \quad ,^{74} \quad (168)$$

and the net heat input is given by

$$Q = \Delta H_{23} \quad , \quad (169)$$

so the cycle efficiency is

$$\eta_i = \frac{-\Delta G_{41}}{\Delta H_{23}} \quad . \quad (170)$$

It can be shown that the sum of the heats of reaction for each process in the cycle is zero, or

$$\Sigma \Delta H = \Delta H_{12} + \Delta H_{23} + \Delta H_{34} + \Delta H_{41} = 0 \quad . \quad (171)$$

But, because there are no reactions occurring in either the heater or the cooler,

$$\Delta H_{12} + \Delta H_{34} = 0 \quad , \quad (172)$$

which leaves only the heats of reaction for the fuel cell and the reverse reaction in the separator as

$$\Delta H_{23} = -\Delta H_{41} \quad . \quad (173)$$

Assuming that the entropy changes occurring in the heating and cooling processes are equal, the efficiency expression is

$$\eta_i = \frac{T_2 \Delta S_{23} + T_1 \Delta S_{41}}{T_2 \Delta H_{23}} = \frac{T_2 - T_1}{T_2} \quad , \quad (174)$$

which is the same as the Carnot efficiency for a heat engine operating between heat reservoirs at T_1 and T_2 .

To produce a refrigerator, the heat engine just described must operate in reverse. The fuel cell must absorb heat from the cold reservoir at T_1 , the products must be heated to T_2 , then the products must be regenerated into the original reactants while rejecting heat to the hot reservoir and must be cooled for reuse in the fuel cell. The operation of a fuel cell in a refrigeration cycle requires that its chemical reaction be endothermic e.g., absorb heat from the surroundings to prevent the cell from getting cold. This also implies that the entropy change be a positive quantity that results in a cycle efficiency greater than 100%. The processes from 1-2 and from 3-4 are in the realm of conventional heat engine cycles. If the products are gases, the process from 1-2 could be an adiabatic compression or simply direct heating to raise the gas temperature to T_2 . Then the process from 3-4 would most probably be a constant enthalpy expansion through a throttling valve. Fuel cells that operate on endothermic chemical reactions are listed in Table XXIX. The candidate reactions occurring at T_1 of 150°C are listed with the heat of reaction, the number of moles of electrons, and the intrinsic efficiency of the medium temperature direct fuel cells.⁷³

The process from 2-3 requires that the fuel cell products be chemically separated while rejecting heat to a high-temperature reservoir. This step depends upon the nature of the reverse reaction, whether or not it is exothermic, and if it can be driven at the higher temperature. In most cases, the reverse reaction requires intermediate compounds or catalysts. In any case, the design of a refrigerator with any of the listed reactions requires extensive knowledge of the chemistry of each particular reaction.

D. Literature Search

A literature survey was made to find information on current research being done in the fuel cell field. References prior to 1965 state that work was primarily concerned with fuel cells using an acid electrolyte. Since then, research has expanded beyond phosphoric acid electrolytes to include molten carbonate and solid oxide electrolytes. There has also been considerably more work done on regenerative fuel cells and systems.

Fig. 44. Temperature-entropy diagram for a regenerative fuel cell.⁷⁴

TABLE XXIX
ENDOTHERMIC FUEL CELL REACTIONS^a

Reactions	ΔG° Kcal/mol	ΔH° Kcal/mol	n	ni
$C_2H_6 + \frac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O$	- 346.99	- 340.66	14	1.019
$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$	- 499.54	- 487.82	20	1.024
$C_4H_{10} + \frac{13}{2}O_2 \longrightarrow 4CO_2 + 5H_2O$	- 651.94	- 634.29	26	1.028
$C_5H_{12} + 8O_2 \longrightarrow 5CO_2 + 6H_2O$	- 804.98	- 781.19	32	1.030
$C_8H_{18} + \frac{25}{2}O_2 \longrightarrow 8CO_2 + 9H_2O$	-1263.72	-1221.70	50	1.034
$C_{10}H_{22}(g) + \frac{31}{2}O_2 \longrightarrow 10CO_2 + 11H_2O$	-1569.62	-1515.37	62	1.036
$C + \frac{1}{2}O_2 \longrightarrow CO$	- 36.09	- 26.31	2	1.372
$C + O_2 \longrightarrow CO_2$	- 94.36	- 94.08	4	1.003
$L_i + \frac{1}{2}Cl_2 \longrightarrow L_iCl(g)$	- 81.38	- 52.01	1	1.565

^aRef. 73, P. 159.

For a fuel cell to operate as part of a refrigeration cycle, the fuel cell reaction must be endothermic, as implied by Bockris in Table XXIX. The refrigeration cycle must be the reverse of the one shown in Fig. 44. Heat must be absorbed by the load from the fuel cell operating at T1, 150°C, then the product gases must be heated in a heat exchanger to T2, 320°C, where they enter a chemical separator or regenerator that separates the product gases into fuel and oxidant streams. The separate streams are then cooled or expanded back to T1 and reintroduced to the fuel cell, thus completing the closed cycle. A summary of each major fuel cell type is made with reference to the candidate reactions identified earlier.

1. Lithium Chloride Cell. The lithium chloride cell has the largest efficiency of any candidate fuel cell reaction, as shown in Table XXIX. The cell consists of a molten lithium electrode, molten lithium chloride electrolyte, and a porous graphite chlorine electrode. The operating temperature must be above the melting point of the electrolyte, which is 608°C. Even though the discharge reaction is exothermic at 150°C, practical operation of a cell requires that the electrolyte be a liquid. Thus the operating temperature is too high for this application.⁷⁷

2. Acid Fuel Cell. Acid fuel cell technology is presently concerned with improving the heat rate, which may require higher operating temperatures. The most common conditions are 205°C and 8 Atm pressure.⁷⁸ Heat rates as high as 7600-7800 Btu/kWh are believed attainable in methane or light distillate systems. It may eventually be possible to develop a direct-internal reforming methanol fuel cell. Because the fuel cell reaction for methanol is exothermic, further development of acid fuel cells using methanol fuels will not provide a suitable component for a refrigeration cycle.

3. Molten Carbonate Fuel Cell. Molten carbonates fuel cells (MCFC) are attractive because the electrolyte is compatible with carbonation fuels.⁷⁹ There has been considerable research in developing MCFC for use in conjunction with electric power generating plants, using coal as a primary fuel. Two major system designs that have been evaluated are the steam resaturation system shown in Fig. 45 and the methane reforming system shown in Fig. 46.⁸⁰ The steam resaturation system eventually sends hydrogen and

Fig. 45. Steam resaturation system.⁷⁹

Fig. 46. Methane reforming system.⁷⁹

carbon monoxide gases to the fuel cell anode operating at 650°C, then the gases pass through a bottoming cycle before being released to the environment. This fuel cell is exothermic and, therefore, unsuitable for a refrigeration cycle. The methane reforming system feeds a mixture of hydrogen and methane to the anode operating at high temperature, with only the hydrogen being converted. This fuel cell is also exothermic.

For both systems, the coal fuel must be gasified and then processed in a reformer that produces simpler compound gases, which result in exothermic fuel cell reactions. Neither system is a suitable component of a refrigeration cycle.

4. Solid Oxide Fuel Cell. The solid oxide fuel cell (SOFC) concept is the most advanced idea considered for fuel cells in making efficient use of fossil fuels.⁸¹ SOFC is simpler, more efficient, and more contaminant-tolerant than any of the other fuel cell systems.⁸² Because of its extremely high operating temperature, 1000°C, it is also the only cell currently capable of direct internal reforming of carbonaceous fuels. A schematic of a SOFC in a power-generating cycle is shown in Fig. 47. Because SOFC operates on exothermic reactions, it is not suitable for use as a component in a refrigeration cycle.

5. Regenerative Fuel Cells. Regenerative fuel cells are classified by regeneration method in the following categories: thermal, electrical, photochemical, and radio chemical. The types most practical for this application are thermal or electrical or a combination of both.⁸³ The above two major categories of regenerative fuel cells can be further subdivided into seven classes. Of these seven classes, five are feasible and two are not feasible. Of the five that are feasible, only three candidates operate in the desired temperature range. They are listed Table XXX.

All of the above systems operate as heat engines, using exothermic reactions and regenerators to separate the product while absorbing heat. Type 3 system performance was shown to be very poor, and the Type 4 system was shown to be not feasible. The Type 7 systems are isothermal thermogalvanic cells with different thermal and electrolytic paths. These systems were shown to have the highest power outputs of all seven thermally regenerative electrochemical systems (TRES).⁸³ Type 7 TRES works on the same principle

Fig. 47. Solid oxide fuel internal reforming system.⁸¹

TABLE XXX

CANDIDATE REGENERATIVE FUEL CELLS^a

Type	Electrolyte	T1	T2
3 or 4	Molten KCl	335	175
6	Solid Electrolyte	184	340
7	Molten PbI	170-400	20-100

^aRef. 82.

as a conventional heat engine with work performed being equivalent to the isothermal expansion of the working electroactive fluid from a high-pressure, high-temperature to a low-pressure zone across the solid electrolyte and its interfaces. The cells are concentration cells in which the electroactive fluid or element is oxidized, with electrons traversing the external circuit and producing electrical work.⁸⁴ The positive ions cross the solid electrolyte and are reduced. The process occurring across the electrolyte is shown schematically in Fig. 48. This fuel cell does not need a chemical regenerator because the fuel is oxidized without undergoing any other chemical changes. The most recent successful work on Type 7 TRES was done with liquid sodium as the working electroactive fluid. The temperature for which sodium has a practical vapor pressure for use in a heat engine is between 500°C and 900°C, a temperature too high for this application. The only liquid metal with an marginal vapor pressure at the given temperature range is mercury. To date, there have only been laboratory cells operated using mercury that showed very low open circuit voltages.⁸³

6. Summary. Each of the fuel cells that uses a hydrocarbon fuel also uses a device called a reformer, which breaks the fuel into simpler compounds, usually carbon monoxide, carbon dioxide, methane and hydrogen gas. The products from the reformer are then fed to the fuel cell. According to Table XXIX, a fuel cell reaction must use fuels with more carbons than methane, such as ethane or propane, to produce an endothermic reaction. The reformer requires a heat input, but its operating temperature is much higher than is the operating temperature of the fuel cell. Even though Bockris suggests that fuel cells using hydrocarbon fuels are endothermic, the fuel cell by itself is exothermic, with the reformer requiring input heat at a temperature that is not suitable for this application. It has been concluded that the use of a fuel cell as a component in a refrigeration cycle is not feasible in the desired temperature range.

XIII. ACTIVE REFRIGERATION DESIGN AND ANALYSIS SUMMARY

A. System Design Results

Table XXXI lists the refrigeration cycles evaluated in the conceptual design and analysis study. Each system design is shown with the candidate refrigerant, the resulting COP, and any relevant information about the cycle.

Of the 25 systems studied, only three are feasible for application to active cooling between reservoir temperatures of 150°C and 320°C. The systems arranged in decreasing order of COP are: (a) acoustic cycle, (b) two-stage vapor compression, and (c) the Brayton cycle with a turbine. The following paragraphs describe results from each calculation.

The acoustic refrigerator showed the highest COP for all systems considered. Helium was used as the refrigerant in a system containing a compressor, a regenerator, a pulse tube, a cold heat exchanger, and two pressure reservoirs. This system has been built and operated successfully at somewhat lower temperatures with no apparent serious problems arising from increases in overall system operating temperatures. Another important advantage results from graceful degradation in the performance of the refrigerator and the instrument electronics, should a gas leak occur.

The two-stage Rankine cycle, using water in the first stage and thermex in the second stage, resulted in the second-best COP. This refrigerator would require two compressors, three heat exchangers, and two expansion valves. A major disadvantage of this system is that any fluid leakage from the refrigerator would not only degrade system performance but would lead to electrical failures in the instrument compartment.

The Brayton cycle using a turbine expander was the only other feasible system choice. This system uses a mixture of helium and xenon as the refrigerant in a cycle that requires only a single-stage compressor, two heat exchangers, and a turbine. Drawbacks to this system result from the mechanical intricacy of the compressor-turbine combination. Leaks from this system would cause graceful degradation of both the refrigerator and the instrument electronics.

The remaining refrigerator designs investigated did not result in COPs high enough to be considered further or they did not have suitable refrigerants.

The refrigerator using a Brayton cycle with a valve in place of the turbine is marginally not feasible because it requires twice the available power input. Possible application might be considered if more than a single conductor, such as a multiplexed application on a multiconductor cable, is available for power input. This cycle is much less intricate and more reliable than is the same cycle with a turbine.

TABLE XXXI
REFRIGERATION CYCLE COP RESULTS

<u>Cycle</u>	<u>Refrigerant</u>	<u>COP</u>	<u>Remarks</u>
<u>Vapor Compression</u>			
Single Stage	Water (ideal)	1.527	Hx-sat. vapor in evaporator, sat. liquid in condenser $P_2 = 1543$ psia, $r = 23$
	(nonideal)	1.087	
	Dowtherm		Not possible as a vapor compression cycle
Single Stage w/Preheater	Water (ideal) (nonideal)	1.302 0.926	Hx-slight amount of superheat at evaporator, slight amount of subcooling at condenser $P_2 = 1543$, $r = 23$
Two Stage	First, water	1.82	Compression ratios $r_1 = 7$, $r_2 = 6.3$ better COP, more complicated
	Second, Thermex (ideal)	1.29	
<u>Brayton</u>			
	Helium with (ideal)	1.40	All cases show compression ratio, $r = 4$ Choice of refrigerant He-Xe based on minimizing physical size of low temperature heat exchanger
	Turbine (nonideal)	0.447	
	Helium with (ideal)	0.189	
	Valve		
	He-Xe (ideal) with turbine	1.40	
	He-Xe (ideal) with valve	0.189	
<u>Joule-Thompson</u>			
	Argon	(--)	No cooling available at these conditions

TABLE XXXI (cont'd)

Cycle	Refrigerant	COP	Remarks
<u>Absorption</u>			
Conventional Absorption Machines	Water-ammonia	(--)	At 300 psia, $51^{\circ}\text{C} < T < 214^{\circ}\text{C}$ solution temperature range
	Lithium-bromide	(--)	$4^{\circ}\text{C} < T < 177^{\circ}\text{C}$ solution temperature range
<u>Thermoelectric</u>			
Single Stage	$\text{Bi}_2\text{Te}_3\text{-Sb}_2\text{Te}_3$ $\text{Bi}_2\text{Te}_3\text{-Bi}_2\text{Se}_3$	(--)	Cannot function as a refrigerator $\Delta T_{\text{max}} = 143.7^{\circ}\text{C}$.
	GeTe-AgSbTe SbTe-PbTe	(--)	Cannot function as a refrigerator $\Delta T_{\text{max}} = 121^{\circ}\text{C}$.
	$\text{PbTe-1\%Na}$ $\text{PbTe-0.055\%PbI}_2$	(--)	Cannot function as a refrigerator $\Delta T_{\text{max}} = 112.8^{\circ}\text{C}$.
Multiple Stage	Same as Single Stage	(--)	No change in ΔT_{max} .
<u>Cascaded T/E</u>			
Max COP	$\text{Bi}_2\text{Te}_3\text{-pair}$ AgSbTe-pair	0.0036	Requires 19.74 amps.
	$\text{Bi}_2\text{Te-pair}$ PbTe-pair	0.071	Requires 19.74 amps.
Max Q	$\text{Bi}_2\text{Te}_3\text{-pair}$ PbTe-pair	0.088	Requires 22.89 amps.
<u>Magnetocaloric</u>			
Carnot cycle Rotating wheel	$\text{Sm}_2\text{Fe}_{17}$ at 368°C Fe_2C	(--)	$T_c = 368\text{K}$, $\Delta T = 10.50$. $T_c = 483\text{K}$, $\Delta T = ?$ (not measured).
	Y_2Fe_{17}	(--)	$T_c = 569\text{K}$, $\Delta T = ?$ (not measured).
	$\text{Y}_2(\text{C}_{.3}\text{Fe}_{.7})_{17}$ Fill-in materials	?	$T = 600\text{K}$, $\Delta T = 7.50$. Volume of refrigerator at 5-1/2-in. o.d., $L = 22\text{ ft}$, is too large and bulky to be practical.

TABLE XXXI (cont'd)

<u>Cycle</u>	<u>Refrigerant</u>	<u>COP</u>	<u>Remarks</u>
<u>Electrocaloric</u>			
	NaNO ₂	?	Not sufficient refrigerant materials to cover ΔT.
	Fill-in material	?	
<u>Fuel cells</u>			
Thermally regenerated fuel cell	Sodium	?	Operating temperature range 500°C < T < 900°C. is too high for this application.
<u>Acoustic</u>			
Pulse tube	Helium (ideal)	2.17	87% of Carnot
Refrigerator	(measured)	1.47	59% of Carnot

All the thermoelectric refrigerators evaluated are not feasible for this application because each requires at least five times the stated maximum power input or more. These methods might be considered feasible for applications requiring much smaller temperature differences at the same cooling loads at the low-temperature reservoir.

The magnetocaloric refrigerator is suited for removal of large heat loads over a very small reservoir temperature difference. It might be useful in an application for long-term cooling at very special reservoir temperatures.

The electrocaloric refrigerants are very similar to the magnetocaloric refrigerants and are not available to cover the temperature range necessary for this application.

The only fuel cell found suitable for use in a regenerative cycle was the thermally regenerative electrochemical system (TRES) fuel cell, using sodium as the electroactive fluid. This system is still in the research stages for use as an engine.

There were no suitable refrigerants found for use in an absorption refrigeration cycle.

The refrigerant choices for use with the Joule-Thompson cycle all resulted in COPs smaller than necessary for this application.

B. Evaluation and Decision Criteria

A rational, unbiased choice between the three candidate systems must be made before proceeding with the detailed engineering design. An evaluation matrix is constructed that includes relevant positive and negative design criteria for comparing the three choices. A decision matrix can be constructed that contains a list of both the controllable and the uncontrollable factors. The controllable factors include the three relevant design alternatives, and the uncontrollable factors include probable future requirements.

A decision between the alternatives can be made in several contexts, which include: (a) decision under certainty, (b) decision under risk, and (c) decision under uncertainty.⁸⁵ A decision made under certainty requires complete and accurate knowledge of the results of each available alternative. That would require a complete engineering design and analysis for each candidate system and would involve the maximum amount of time, effort, and cost.

A decision made under risk requires fewer data than one made under certainty but implies some knowledge of the probability of the success of occurrence of each end result. For this study, the conceptual designs and analyses provide a large quantity of consistent data for each system. The chapter describing the state-of-the-art reveals several trends that are likely to continue and are the basis for defining the uncontrollable factors and estimating their probabilities. A decision between systems can be made after selecting a principle-of-choice.

The last decision type is one made under uncertainty, which is very similar to a decision made under risk, but exists when there is no knowledge of the probability of the occurrence of each end result. The conceptual designs and the review of the state-of-the-art were carried out specifically to avoid this type of decision.

There are numerous principles-of-choice. They are based upon the following criteria: (a) maximizing benefits, (b) maximizing expectations, (c) most probable future, (d) aspiration level, (e) equal probability, (f) conservatism, and (g) regret.⁸⁵ The principles most appropriate for a decision under risk are (b) through (d). The most commonly used

TABLE XXXII
SYSTEM EVALUATION MATRIX

Design Criteria	I	Acoustic		Brayton		Rankine	
		S ₁	S ₁ XI	S ₂	S ₂ XI	S ₃	S ₃ XI
<u>Postive</u>							
a) Probability of meeting design specifications	10	4	40	5	50	5	50
b) Adaptability to changes in refrigeration load	8	5	40	3	24	1	8
c) Degradation or failure mode	8	5	40	5	40	2	16
d) Adaptability to changes in B.C.(spell out)	5	5	25	4	20	3	15
e) Serviceability	2	4	<u>8</u>	3	<u>6</u>	1	<u>2</u>
			153		140		91
<u>Negative</u>							
a) Interference w/measurement	10	2	-20	3	-30	4	-40
b) Production cost	2	2	- 4	3	- 6	5	-10
c) Maintenance cost	3	2	<u>- 6</u>	2	<u>- 6</u>	4	<u>-12</u>
			-30		-42		-62
			<u> </u>		<u> </u>		<u> </u>
			123		98		29

TABLE XXXIII
DESIGN DECISION MATRIX

System Design Criteria	Higher T_{hi}		Smaller O.D.		Longer	
	S_1	$p_1=0.6$	S_2	$p_2=0.25$	S_3	$p_3=0.15$
<u>Acoustic</u>						
a) Probability of meeting new specs	10	6	10	2.5	8	1.20
b) Difficulty in rebuilding for new specs	- 2	-1.2	- 2	-0.5	-1	-0.15
		_____		_____		_____
		4.8		2.0		1.05 7.85
<u>Brayton</u>						
a) Probability of meeting new specs	9	5.4	6	1.5	8	1.20
b) Difficulty in rebuilding for new specs	- 4	-2.4	- 3	-0.75	-1	-0.15
		_____		_____		_____
		3.0		0.75		1.05 4.80
<u>Rankine</u>						
a) Probability of meeting new specs	7	4.2	4	1.0	8	1.20
b) Difficulty in rebuilding for new specs	- 6	-3.6	- 5	-1.25	-8	-0.15
		_____		_____		_____
		6.0		-0.25		1.05 1.40

principle-of-choice is based upon maximizing expectations, which requires selecting the alternative with the lowest expected cost of the highest expected benefit. Another common principle is the "most probable future." This principle considers only the most probable outcome and ignores all other outcomes and their consequences. The "aspiration level" is the third widely used principle and involves selection of a desired aspiration level or result, L. A choice is made from the alternative that has the highest probability that the cost will be less than L or the benefit will be greater than L. This process is most effective when used among alternatives that are very expensive or are difficult to define. The principle-of-choice used for this study will be maximizing expectations.

Each of the candidate systems is rated using an evaluation matrix, shown in Table XXXII, that includes relevant positive and negative comparison criteria. The evaluation is based upon the design criteria stated in a previous chapter. A decision matrix shown in Table XXXIII is constructed from the three candidate designs with a comparison of the three most probable extensions to the stated design criteria and the positive and negative aspects of meeting the extended criteria.

C. Selected System

Results of the evaluation and the decision process show that the acoustic refrigeration system is the best choice for proceeding with detailed engineering design and analysis. It is also the most likely system to meet any or all of the extended design criteria.

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