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Isotopic Purification of Helium by Differential Distillation Below the Lambda-Point

UNITED STATES DEPARTMENT OF THE INTERIOR

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Isotopic Purification of Helium by Differential Distillation Below the Lambda-Point

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ISOTOPIC PURIFICATION OF HELIUM BY DIFFERENTIAL DISTILLATION BELOW THE LAMBDA-POINT

by

Philip C. Tully [1]

ABSTRACT

The Bureau of Mines, in a continuing effort to improve processes and methods of helium purification, has developed a differential distillation method for removing helium-3 from helium-4. Differential distillation at 4.2 to 1.6 K was used to reduce the helium-3 in helium-4 from about 200 to less than 1 part per billion. The results from four stills ranging in size from 1 to 25 liters are reported. The method has the potential to be adapted to commercial-scale separations.

INTRODUCTION

As required by the Helium Act, Public Law 86-777, the Secretary of the Department of the Interior is authorized to maintain and operate helium production and purification plants. In pursuit of this mission, the Bureau of Mines is engaged in increasing the purity of the helium product. The ultimate purification of helium-4 requires removal of the helium-3 isotope. All impurities, except helium-3, can be removed by freezeout or adsorption at liquid helium temperatures. The helium-3 free product can be useful as a coolant in gas-cooled nuclear reactors, where helium-3 is changed to radioactive tritium, and as a pure isotope for research. The work described in this report was carried out at the Bureau of Mines Helium Operations Facility, Amarillo, Tex.

Previous work in the separation of helium-3 from helium-4 has been directed toward producing helium-3 rather than toward increasing the purity of helium-4. The helium-3 is used to study its physical properties and as a refrigerant.

Some of the more widely known methods of separating the helium isotopes are the "superleak" (4-5),[2] a leak so small that only a superfluid can get through; the "heat-flush" (15, 25), flow of a superfluid to a small heat source; thermal diffusion (1, 13, 17-18, 24); and fractional distillation of

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[1] Chemical engineer.

[2] Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

a feedstock preconcentrated to several percent helium-3 (10, 32); or combinations of these methods (14, 19, 21). Rollin and Hatton (23) pointed out that helium-3 could be concentrated by evaporation of liquid helium below the lambda-point, the temperature (2.17 K) at which liquid helium becomes superfluid He II. Production of helium-3 has also been achieved using thermal diffusion and distillation.

The production of helium-4 containing reduced amounts of helium-3 on a laboratory scale using the superleak is pointed out in a recent paper by Mezhov-Deglin (20), as well as in Hildebrandt's patent (11), although the product quality is not reported. Pure helium-4 containing <1 part per billion by mole (ppb) helium-3 has not been reported. It is believed that the differential distillation process described herein can be used to produce helium-4 free of helium-3 in commercial quantities. (See (22) for a discussion of differential distillation.)

The separation described in this report is carried out using a batch-type differential distillation to produce helium containing from 17 ppb to <1 ppb helium-3. The separation relies on the advantageous vapor-liquid distribution of helium-3 occurring below 2.17 K (fig. A-1). Separations described in the literature generally rely on other phenomena (such as the superleak), require more precise temperature control, and are less suited to industrial production than the process described.

ACKNOWLEDGMENTS

The author thanks Harold L. Rhodes, chemist, for his assistance in the area of instrumentation, apparatus construction, and sampling procedures; Elmer T. Suttle, supervisory chemist, for analyzing the samples; and Robert E. Wood, chemical engineer, for carrying out the first differential distillation calculation. All are with the Unit of Technical Services, Helium Operations, Bureau of Mines, Amarillo, Tex.

EXPERIMENTAL APPARATUS

The essential components of the differential-distillation apparatus are shown schematically in figure 1. They are a source of liquid helium, a helium dewar or still (1), a vacuum pump (6), a compressor (11), a liquid nitrogen charcoal adsorber (12), and product storage containers (13).

The still contains a small, 100-watt cartridge heater (2), which is connected to an external variable-voltage power supply (3). A 1/8-watt, 100-ohm carbon resistance thermometer (not shown) is also in the still. It has a 5-microampere power supply and digital voltmeter readout.

A pressure indicator (4) and vacuum-tight, low-pressure (<5 psig) relief valve (5) are added to protect the still.

Four stills of 1- to 25-liter capacity were used to determine the effects of batch size on product quality, yield, and run duration. Different vacuum pumps and compressors were used with different stills as follows:

1. A 1-liter glass dewar immersed in liquid nitrogen in another glass dewar was used for the still in runs 1-3. An external infrared lamp was used as a heater. The thermometer was not installed in this first still. A 600-liter-per-minute (l/min) vacuum pump was connected to the still by 1-1/4-inch copper pipe, 1-inch hard-drawn copper tubing, and a rubber stopper. A 20-l/min vacuum pump served as a 38-psig discharge product compressor.

2. A 10-liter stainless steel helium dewar with a liquid-nitrogen-cooled radiation shield was used for runs 4-7. The suction of two 35-scfm compressors was used to reduce system pressure and temperature. A 600-l/min vacuum pump was added to achieve vacuums below 50 torr. A 250-psig discharge 35-scfm compressor was used for product handling.

3. A 15-liter liquid-nitrogen-shielded helium dewar was used for runs 8-10. One 600-l/min and two 140-l/min vacuum pumps were connected to the still by 2-inch corrugated copper tubing. A diaphragm compressor boosted the discharge of the 250-psig compressor in paragraph 2 to 1,500 psig.

4. A 25-liter 7-1/2-inch OD, stainless steel, liquid nitrogen dewar inside a 40-liter, 9-inch-ID, nitrogen dewar was used as a still in runs 11-22. All other components were the same as in paragraph 3.

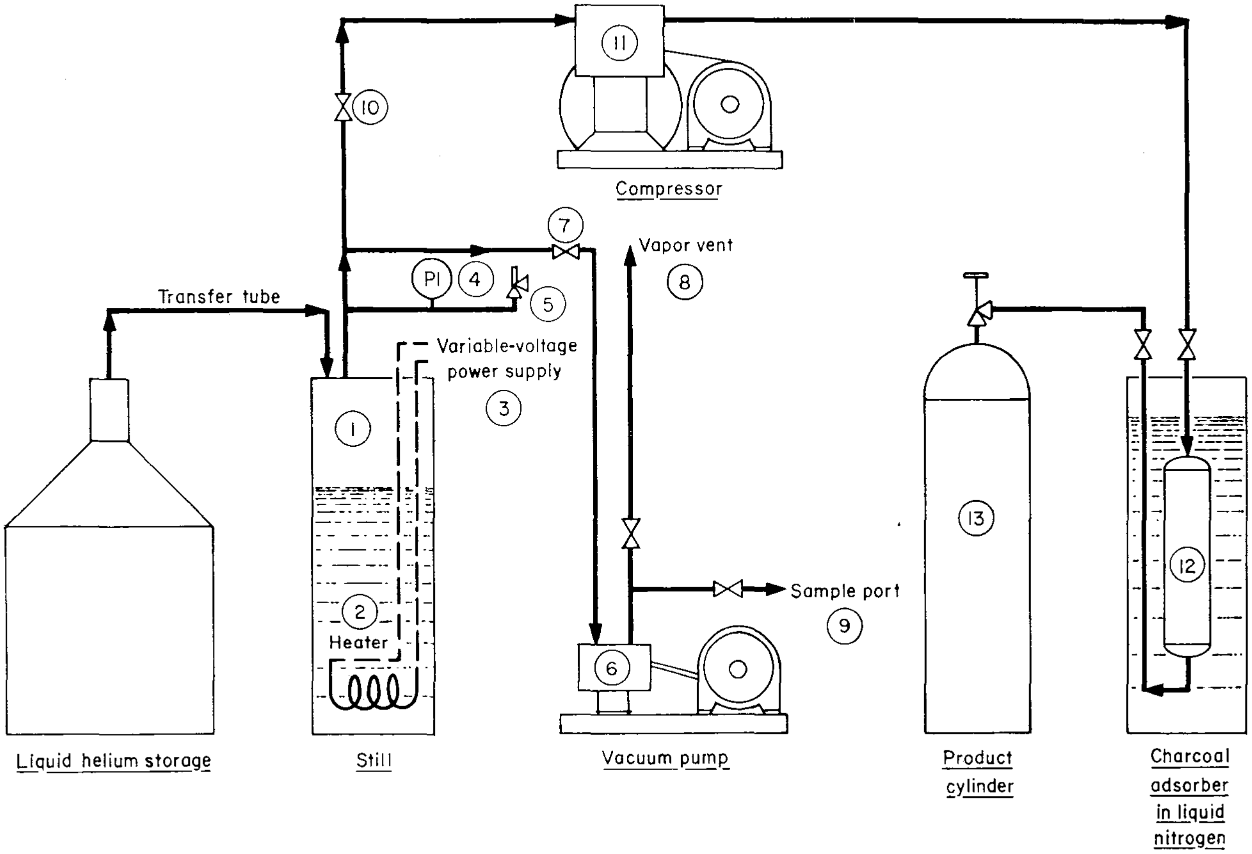

FIGURE 1. - Schematic diagram of differential distillation of helium-3 from helium-4.

The charcoal adsorber contains about 4 liters of coconut charcoal.

EXPERIMENTAL PROCEDURE

A run was started by transferring a batch of liquid helium into the still. The still was filled only to about two-thirds capacity to promote smoother and more efficient operation. The still was sealed with valves 7 and 10 closed. After starting the vacuum pump (6), the evacuation was started slowly by taking about 10 minutes to fully open valve (7). This avoided excessive boilup, entrainment, and loss of cooling. The vapor withdrawn from the still by the vacuum pump was vented to the atmosphere through the vapor vent (8).

The distillation was monitored by observing pressure, temperature, and composition. For pressure, the output of a self-balancing, servo-operated, digital quartz bourdon tube pressure indicator (4) was displayed on an adjustable-range strip chart recorder. The absolute pressure was determined by applying barometric and calibration corrections. For temperature, the voltage drop across the carbon resistance thermometer was displayed on a digital voltmeter. The thermometer was calibrated at the liquid nitrogen and liquid helium points using the vapor pressure equations of Strobridge (27) and Van Dijk (30), respectively, to determine the temperature. The Clement equation (2, 16) was used to determine the two thermometer constants and the temperature as a function of the voltage drop. Comparison of the temperatures determined from the vapor pressure with those from the thermometer showed a difference of 0.02 to 0.03 K, as observed by Lindenfeld (16).

The composition of the vapor from the still was determined by mass spectrometer analysis of a sample collected at the sample port (9). The spectrometer was modified especially to determine helium-3 in helium-4 in the parts-per-billion range. The minimum detectable limit was 0.5 ppb with a precision of 10 percent relative. Results were obtained in 20 minutes.

The decision to terminate each run was based on the results of the vapor analyses. The liquid composition was estimated using the K-value.

Some runs were made to produce a product containing <1 ppb helium-3. Other runs were made to less stringent specifications. After the decision was made, a terminal sample was usually taken immediately before the vacuum valve (7) was closed and the pump shut off.

The still was rapidly restored to 1-2 psig by vaporizing a small portion of the remaining liquid using the heater (2). The compressor (11) was started and the valve (10) opened. The heater voltage was adjusted manually to maintain the suction pressure between 1 and 2 psig. The compressor discharge was passed through the liquid nitrogen charcoal adsorber (12) and accumulated in the product cylinders (13).

DISCUSSION OF RESULTS

The results of the vapor analyses from runs 1-3 made in the 1-liter glass dewar are presented in table 1 and plotted in figure 2. They show that the concentration of helium-3 in the vapor reaches a maximum (~500 ppb) slightly below the lambda-point (indicated by He II), and declines to <1 ppb as the differential distillation continues. Comparison of the last vapor analysis of run 1 (<1 ppb) with the product analysis (also <1 ppb) shows that the depletion of the helium-3 in the vapor is caused by the depletion in the liquid. Comparison of the same analyses for run 2 yields an apparent K-value ($K = y/x$, where y and x are the helium-3 concentrations in the vapor and liquid, respectively) at run's end of 16.2. In run 3, the product has a higher helium-3 content (2 ppb) than the last vapor sample (<1 ppb). This is attributed to residual contamination in the first of two containers used to store the product.

TABLE 1. - Analyses of vapor and product, 1-liter glass dewar

Run	Duration, min	He^3 analyses, ppb	He^4 product, scf
1	1	340	-
	2	465	-
	9	171	-
	27	<1	-
	-	[1]<1	6
2	1	224	-
	6	239	-
	8	186	-
	9	137	-
	11	81	-
	-	[1]5	5
3	8	165	-
	10	86	-
	13	22	-
	16	7	-
	19	1	-
	22	<1	-
	-	[1]2	6

[1] Product analysis.

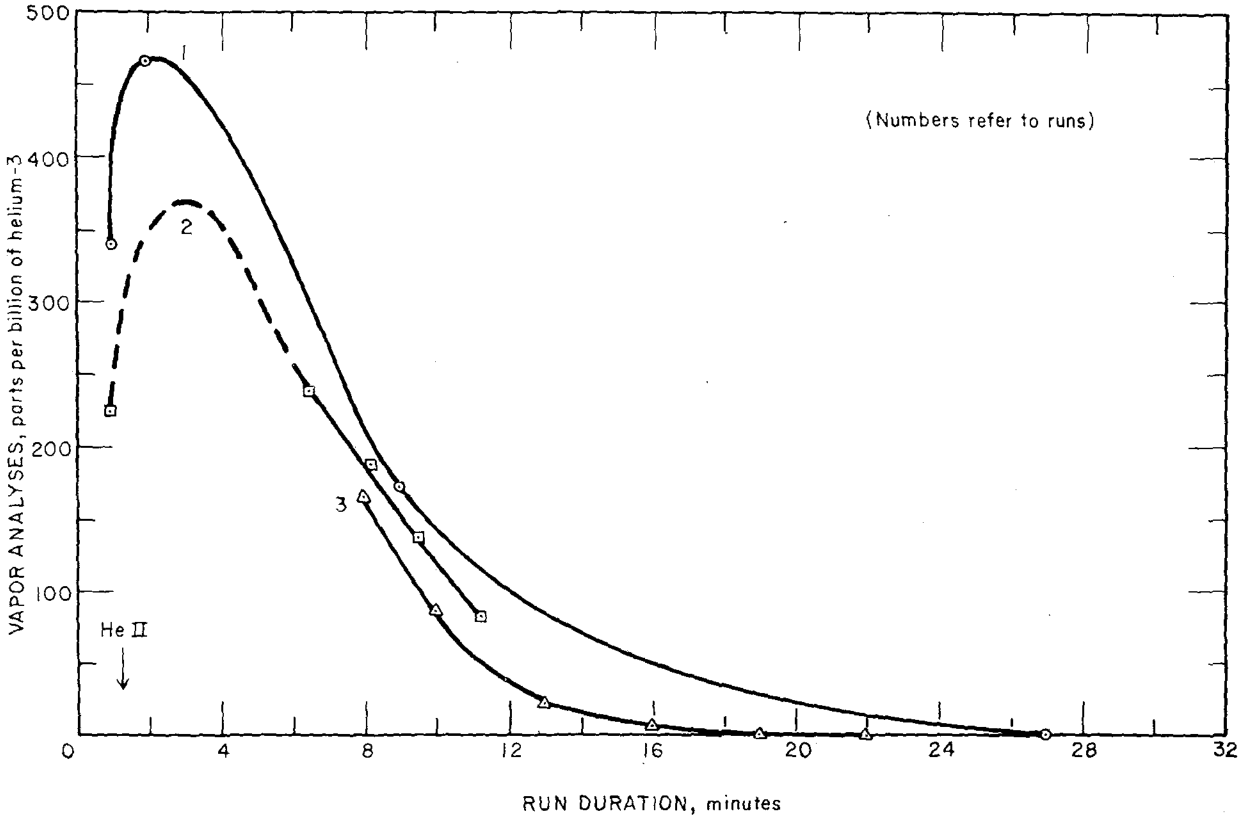

FIGURE 2. - Vapor analyses versus run duration, 1-liter glass dewar.

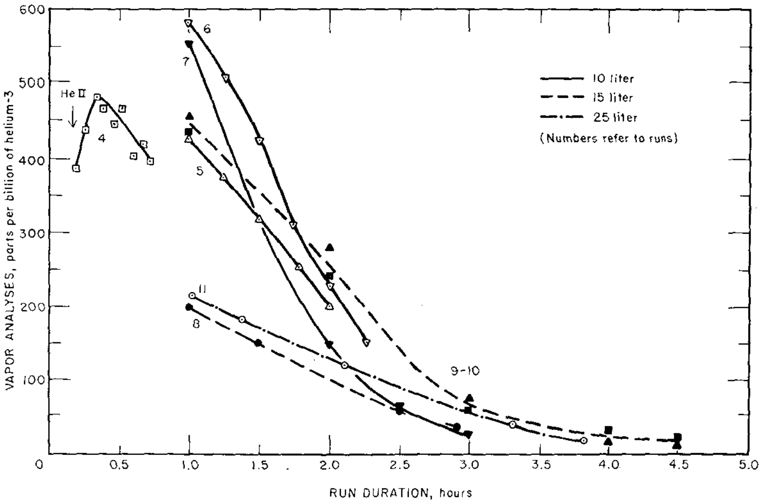

FIGURE 3. - Vapor analyses versus run duration, stainless steel dewars.

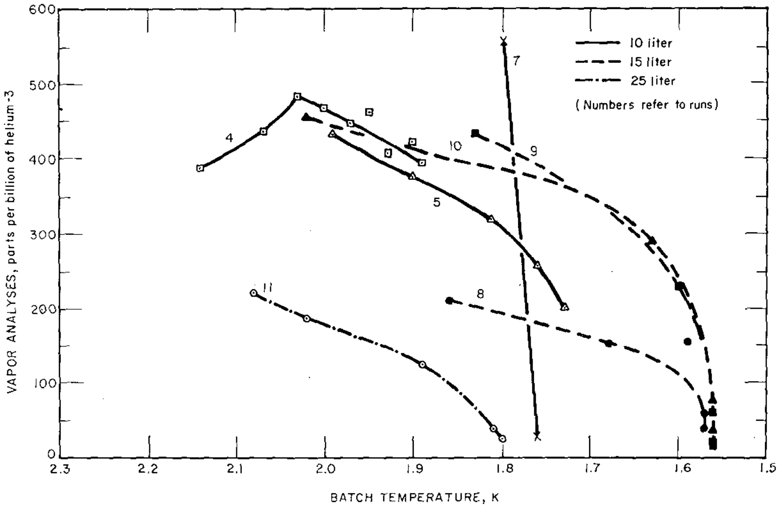

FIGURE 4. - Vapor analyses versus batch temperature, stainless steel dewars.

The results of runs 4-7 made in a 10-liter stainless steel dewar are presented in table 2 and portrayed in figures 3 and 4. Referring to figure 3, run 4 confirmed that the maximum He^3 composition of the vapor occurred slightly below the lambda-point. To reduce the total number of analyses, no more samples were taken during the initial part of subsequent runs. Also, the goal of the investigation was shifted from obtaining a product containing no detectable helium-3 to achieving higher yields and production rates, accepting a higher helium-3 content in the product as a consequence.

Comparing runs 5, 6, and 7, the effect of eliminating leaks in the vacuum system is seen. One vacuum-tight valve was installed between runs 5 and 6, and two more between runs 6 and 7. Run 7 has the best rate of helium-3 removal, as indicated by the slope, because the ratio of vacuum pump capacity to batch size is 9.1 scfm per liter. (Runs 1-3 had a ratio of 21.2, but they were strictly qualitative.)

TABLE 2. - Analyses of vapor and product, 10-liter stainless steel dewar

Run	Duration, hr	He^3 analyses, ppb	Temperature, K	He^4 product, scf
4	0:11	386	2.14	-
	0:15	437	2.07	-
	0:19	480	2.03	-
	0:23	465	2.00	-
	0:27	449	1.97	-
	0:31	461	1.95	-
	0:35	405	1.93	-
	0:39	416	1.90	-
	0:43	395	1.89	-
	-	(1)	-	(1)
5	1:00	429	1.99	-
	1:15	378	1.90	-
	1:30	320	1.81	-
	1:45	257	1.76	-
	2:00	201	1.73	-
	-	[2]7	-	120
6	1:00	581	(3)	-
	1:15	506	(3)	-
	1:30	429	(3)	-
	1:45	313	(3)	-
	2:00	230	(3)	-
	2:15	150	(3)	-
	-	[2]7	-	160
7	0:30	(4)	1.93	-
	1:00	554	1.80	-
	2:00	144	1.78	-
	2:30	67	1.77	-
	3:00	31	1.76	-
	-	[2]2	-	200

[1] Not enough liquid left to vaporize.
[2] Product analysis.
[3] Open circuit.
[4] No sample taken simultaneously with temperature data.

The results of runs 8-10, made in a 15-liter helium dewar with a 1-inch-ID by 18-inch-long tail section, are presented in table 3 and shown also in figures 3 and 4. This dewar was used to attain lower temperatures than previously established (1.56 versus 1.73 K). It was anticipated that the higher K-value (24 versus 17) at the lower temperature would increase the amount of helium-3 vaporized and expedite the separation. This did not materialize. Instead, the vapor compositions became asymptotic to about 25 ppb (39, 15, and 22, respectively) and the product compositions to about 7 ppb. This might have been the result of reducing the ratio to 2.1 scfm per liter. It is also possible that the shape of the tail section might have diminished the effect of the heat flush on the separation.

TABLE 3. - Analyses of vapor and product, 15-liter stainless steel dewar

Run	Duration, hr	He^3 Analyses, ppb	Temperature, K	He^4 Product, scf
8	1:00	209	1.86	-
	1:30	153	1.68	-
	2:30	57	1.57	-
	2:54	39	1.57	-
	-	[1]8	-	220
9	1:00	434	1.83	-
	2:00	233	1.60	-
	3:00	58	1.56	-
	4:00	20	1.56	-
	4:30	15	1.56	-
	-	[1]7	-	160
10	1:00	454	2.02	-
	2:00	287	1.63	-
	3:00	76	1.56	-
	4:00	34	1.56	-
	4:30	22	1.56	-
	-	[1]7	-	(2)

[1] Product analysis.
[2] Lost.

Referring to figure 4, it is seen that the highest rates of change of composition with respect to temperature are achieved at the lowest temperature or with small batches and high-capacity vacuum systems (run 7).

The results of runs 11-22 are given in table 4. This group of 12 runs in the 25-liter dewar was made to determine the effect of product quality specifications on yield, as shown in figure 5, and the effect of run duration on product analyses and yield, as shown in figure 6. Batch sizes were varied from 5 to 22 liters. Run durations ranged from 1 hour to 4 hours 26 minutes. In figure 5, it is seen, for systems having pumping ratios similar to this one, that specified quality down to about 10 ppb has little effect on reducing the yield. Below 10 ppb, each reduction of 1 ppb will reduce the yield by about 3 percent. From figure 6 it is seen that each reduction of 1 ppb will require an additional 12 minutes of distillation.

TABLE 4. - Analyses of vapor and product, 25-liter stainless steel dewar

Run	Batch, liters	Duration, hr	Analyses He^3, ppb	Temperature, K	He^4 product, scf	Yield, pct
11	15	1:02	217	2.08	-	-
		1:22	185	2.02	-	-
		2:06	117	1.89	-	-
		3:19	39	1.81	-	-
		3:50	23	1.80	-	-
		-	[1]7	-	130	32
12	12	0:41	(2)	2.17	-	-
		1:25	122	2.09	-	-
		2:05	52	2.04	-	-
		2:34	(2)	2.02	-	-
		3:00	10	2.00	-	-
		3:30	5	1.99	-	-
		-	[1]1	-	130	40
13	18	0:18	(2)	2.41	-	-
		0:26	(2)	2.19	-	-
		0:30	(2)	2.17	-	-
		0:35	270	2.15	-	-
		0:59	252	1.98	-	-
		1:30	(2)	1.85	-	-
		1:46	(2)	1.80	-	-
		2:03	97	1.76	-	-
		3:01	23	1.74	-	-
		4:00	2	1.71	-	-
		-	[1]<1	-	120	25
14	22	0:38	(2)	2.17	-	-
		1:00	211	2.07	-	-
		1:36	(2)	1.92	-	-
		2:04	109	1.84	-	-
		2:38	66	1.78	-	-
		-	[1]2	-	170	29
15	14	0:30	(2)	2.17	-	-
		1:00	358	1.94	-	-
		1:25	(2)	1.80	-	-
		1:30	162	1.78	-	-
		2:06	71	1.72	-	-
		2:50	5	1.72	-	-
		-	[1]<1	-	130	35

See footnotes at end of table.

TABLE 4. - Analyses of vapor and product, 25-liter stainless steel dewar--Continued

Run	Batch, liters	Duration, hr	Analyses He^3, ppb	Temperature, K	He^4 product, scf	Yield, pct
16	14	1:20	239	2.17	-	-
		1:37	258	2.07	-	-
		2:02	190	1.87	-	-
		2:16	174	1.80	-	-
		3:00	66	1.70	-	-
		-	[1]2	-	140	37
17	5	0:16	(2)	2.64	-	-
		0:24	(2)	2.17	-	-
		0:31	125	1.99	-	-
		0:42	(2)	1.85	-	-
		0:50	(2)	1.79	-	-
		1:00	5	1.73	-	-
		-	[1]<1	-	35	26
18	17	0:41	(2)	2.17	-	-
		1:01	375	2.04	-	-
		1:19	328	1.93	-	-
		1:57	(2)	1.78	-	-
		2:00	172	1.77	-	-
		-	[1]5	-	270	60
19	17	0:24	(2)	2.90	-	-
		0:40	(2)	2.27	-	-
		0:48	(2)	2.17	-	-
		1:01	405	2.10	-	-
		1:35	310	1.87	-	-
		-	[1]15	-	270	60
20	16	0:15	(2)	3.04	-	-
		0:36	(2)	2.17	-	-
		1:02	391	2.00	-	-
		1:16	(2)	1.89	-	-
		1:30	284	1.82	-	-
		-	[1]17	-	270	63
21	18	0:25	(2)	2.50	-	-
		0:40	(2)	2.17	-	-
		1:10	(2)	1.97	-	-
		1:56	(2)	1.76	-	-
		2:00	154	1.74	-	-
		-	[1]7	-	260	54
22	19	0:38	(2)	2.17	-	-
		2:30	45	1.74	-	-
		-	[1]5	-	270	53

[1] Product analysis.

[2] No sample taken simultaneously with temperature data.

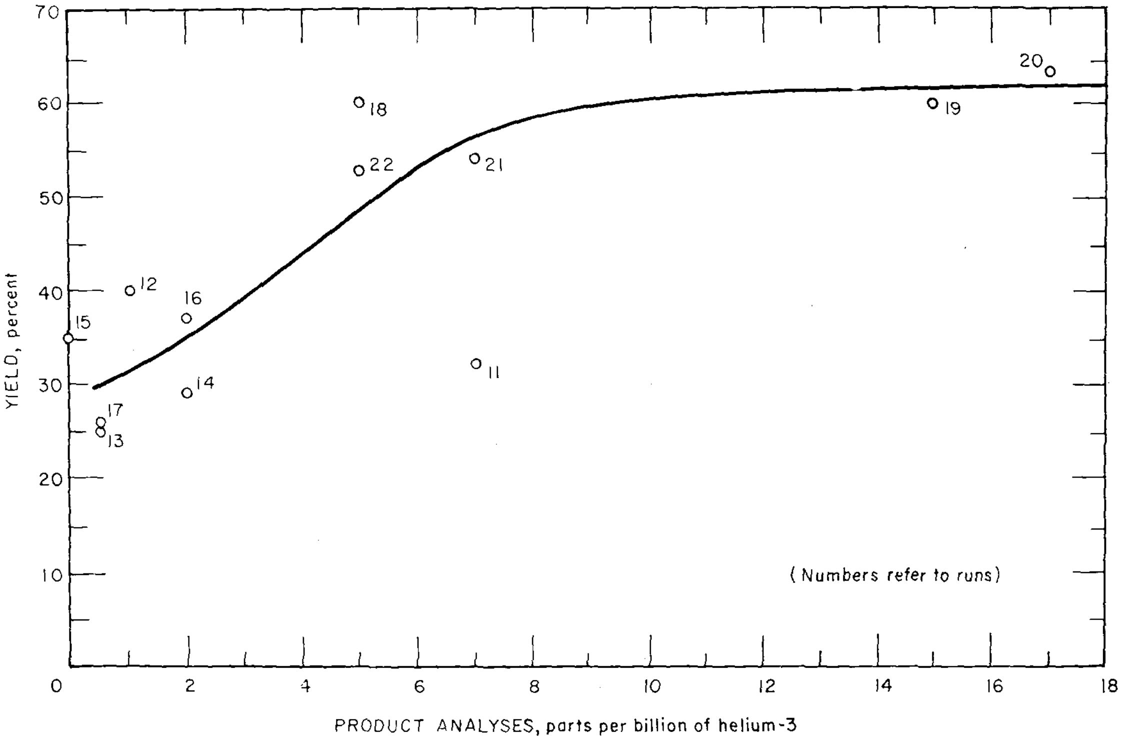

FIGURE 5. - Yield versus product analyses, 25-liter stainless steel dewar.

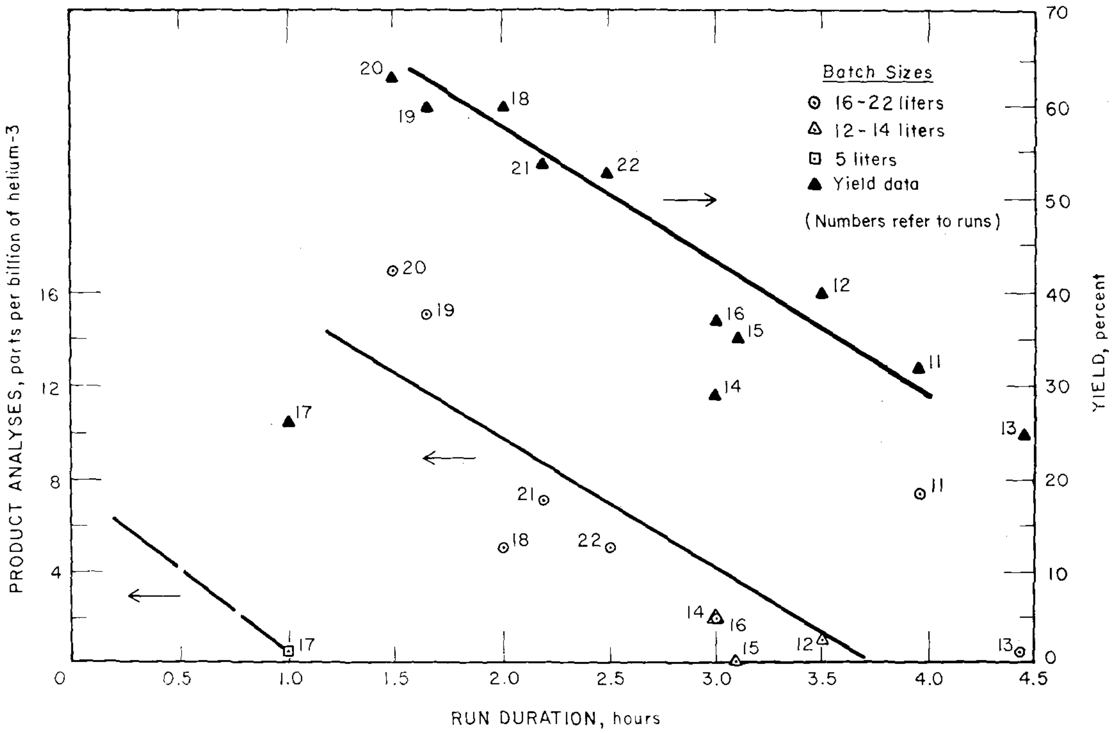

FIGURE 6. - Product analyses and yield versus run duration, 25-liter stainless steel dewar.

Differential distillation calculations were carried out to compare theoretical and actual performance. Details of the calculations are given in the appendix. The results are shown in figure 7. Calculated and actual results for run 11 for the portion shown are seen to agree within 75 ppb. For run 11, the calculated heat leak of 0.1138 joule per 0.01° used in the calculation is the same percentage of a 1-mole batch that the observed heat leak boiloff of 35 scfm for this dewar arrangement was of the 15-liter batch. Actual compositions are better because of the benefits of the heat-flush effect. The calculated yield of 39 percent for a 23-ppb vapor is better than the actual figure of 32 percent. This might be caused by inefficient utilization of the refrigeration produced by the evaporating liquid.

For run 13, the agreement between calculated and actual quality is about the same as it is for run 11.

A yield of 53 percent was calculated for run 21 for a 154-ppb vapor compared with an observed value of 54 percent.

For an ideal no-heat-leak dewar arrangement, the calculations show that the boilup would be insufficient to effectively remove the helium-3. The calculations also show that it would require 24.5 percent of the batch to reach

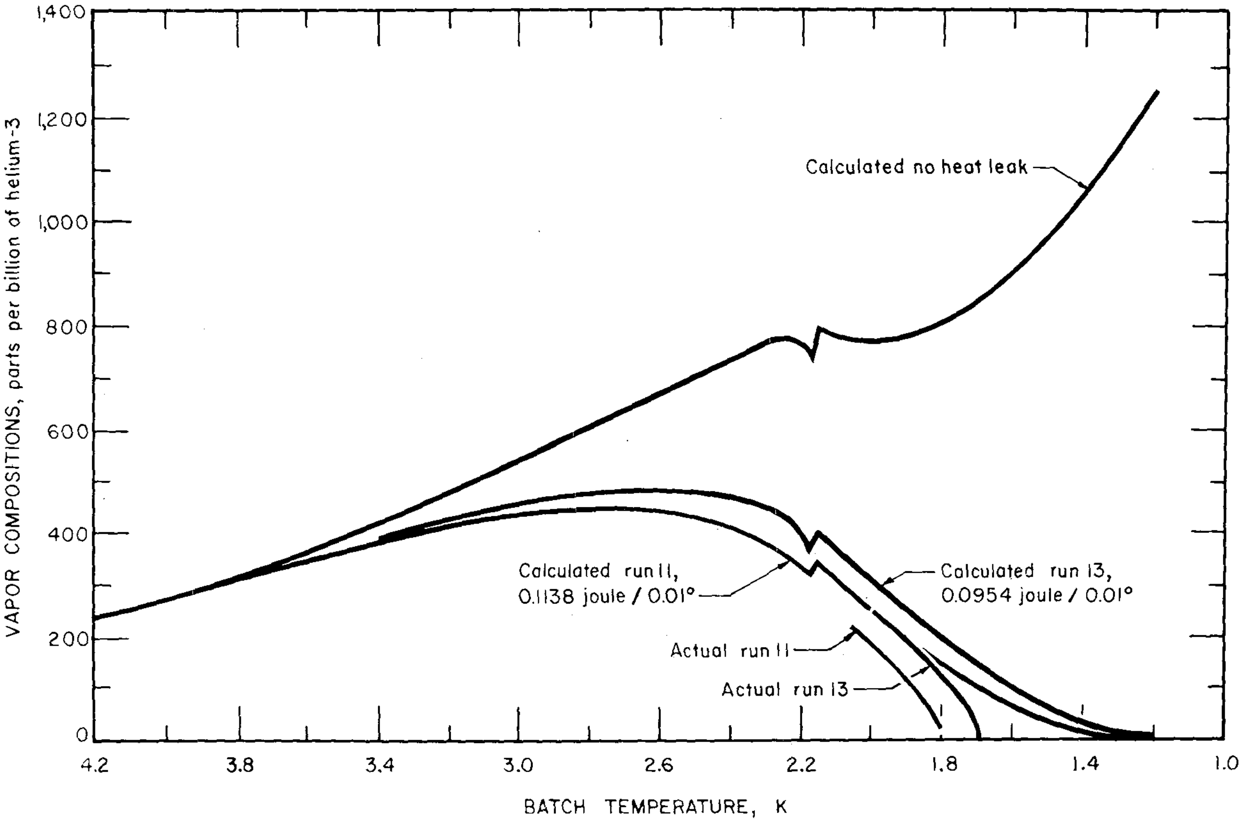

FIGURE 7. - Calculated and actual vapor compositions versus batch temperature for differential distillation of helium-3 from helium-4.

the lambda-point. When this is added to the 15-percent shrinkage due to the density increase from 4.2 to 2.17 K, it agrees with the observations made in the 1-liter glass dewar.

CONCLUSIONS

The removal of helium-3 from liquid helium by differential distillation has been demonstrated on a laboratory scale. The process was applied to batches from 1 to 22 liters. From this, it is believed that the process can be applied to much larger batches of industrial significance.

It is an important design consideration that the capacity of the vacuum system be large enough to obtain sublambda temperatures within a reasonable time. In this temperature range the advantages of superfluidity and high K-values are utilized. Based on runs 8-10, 2 scfm per liter of liquid helium and an ultimate vacuum of several micrometers should be sufficient for dewars with normal boiloff. Higher yields and shorter run durations are possible with vacuum systems having pumping ratios of 10 (runs 4-7), or even 20 (runs 1-3), scfm per liter.

The differential distillation calculations represent the actual performance rather well, considering that no superfluid effects were taken into account.

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APPENDIX

The parameters of differential distillation are expressed mathematically in the Rayleigh equation (22)

$$\ln \frac{W}{W_0} = \int_{x_0}^{x} \frac{dx}{y-x}, \tag{A-1}$$

where W_0 = original quantity of the liquid mixture,

$W = W_0 - dw$ = quantity of mixture remaining after vaporization of an incremental amount dw,

x_0 = original fraction of a component in W_0,

x = fraction of a component in W,

$dx = x_0 - x$,

and y = fraction of a component in the vapor produced.

By expressing y in terms of x, $y = Kx$, and assuming K is constant with respect to x, equation A-1 can be integrated analytically to

$$\frac{x}{x_0} = \left(\frac{W}{W_0}\right)^{K-1}. \tag{A-2}$$

For this case of the vaporization of liquid helium, the amount vaporized is

$$dw = dTC_s W_0/L_v + Q/L_v, \tag{A-3}$$

where dT = an incremental temperature drop of W_0, which supplies part of the heat of vaporization,

C_s = specific heat at the saturated vapor pressure,

L_v = latent heat of vaporization,

and Q = heat leak into the liquid, which supplies the remainder of the heat of vaporization.

Assuming values for dT, W_0, and x_0, using expressions of C_s, L_v, and K as functions of T, equations A-3 and A-2, and $y = Kx$, it is possible to calculate y and x for each increment until a given T is reached. A material balance was also calculated by summing the increments of helium-3 lost in vaporization, ydw, and the helium-3 remaining in the liquid, xW, and comparing the sum to the original amount of helium-3 in the batch, x_0W_0.

Starting values of 0.01°, 1 mole, and 200 ppb were assumed for dT, W_0, and x_0, respectively.

The specific heat data of Hill and Lounasmaa (12) were represented as a series of eight straight lines on semilogarithmic graph paper. The equations for these lines are--

$$
\begin{aligned}
C_s &= 0.045169\ (21.3751)^T \text{ joules/deg-mole} && (1.20 \leq T \leq 2.00)\\
&= 0.0071206\ (53.5601)^T && (2.01 \leq T \leq 2.14)\\
&= 5.24673 \times 10^{-11}\ (3.25946 \times 10^{5})^T && (2.15 \leq T \leq 2.17)\\
&= 5.65104 \times 10^{42}/(7.69697 \times 10^{18})^T && (2.18 \leq T \leq 2.20)\\
&= 240564/(79.7046)^T && (2.21 \leq T \leq 2.32)\\
&= 21.6805/(1.404)^T && (2.33 \leq T \leq 2.60)\\
&= 4.1507\ (1.342)^T && (2.61 \leq T \leq 3.19)\\
&= 2.10136\ (1.66209)^T && (3.20 \leq T \leq 4.20)
\end{aligned}
$$

The latent heat of vaporization data of Van Dijk and Durieux (29) have been approximated by--

$$
\begin{aligned}
L_V &= (16)(T-1.0) + 80 \text{ joules/mole} && (1.20 \leq T \leq 1.74)\\
&= 92 && (1.75 \leq T \leq 3.50)\\
&= 92 - (16)(T-3.5) && (3.50 \leq T \leq 4.20)
\end{aligned}
$$

For K-data above the lambda-point, the values of C_V/C_L reported by Fairbank, Lane, Aldrich, and Nier (8) were used. (For their concentrations of helium-3 in natural liquid helium, $K \cong C_V/C_L$.) It was not advisable to use their data or that of others (3, 6, 9, 28) below the lambda-point because of the composition errors caused by sampling the inhomogeneous superfluid.

Below the lamda-point, the $\Delta P/P$ values of Sommers (26) at 0.58 percent helium-3 were used to calculate the K-values using his equation 2. Subsequent papers (7, 31) are in reasonable agreement with Sommers. At this concentration, $K \neq C_V/C_L$. The results were--

T	$\Delta P/P$	$C_V C_L$	K
2.172	.0338	6.57	6.36
2.066	.0434	8.38	8.04
1.957	.0553	10.7	10.09
1.847	.0717	13.9	12.91
1.749	.090	17.6	16.04
1.658	.116	23.1	20.50
1.612	.120	23.9	21.13
1.517	.156	32.2	27.27
1.405	.196	42.2	34.05
1.395	.196	42.2	34.04
1.272	.244	55.5	42.18

The two sets of data were represented by--

$$K_{He^3} = 592.258/7.8002^{T} \qquad (1.2 \leq T \leq 2.17)$$

and

$$= 38.6948/2.29699^{T} \qquad (2.18 \leq T \leq 4.8)$$

and are plotted in figure A-1.

The calculations were programed in an iterative scheme and carried out on a digital computer.

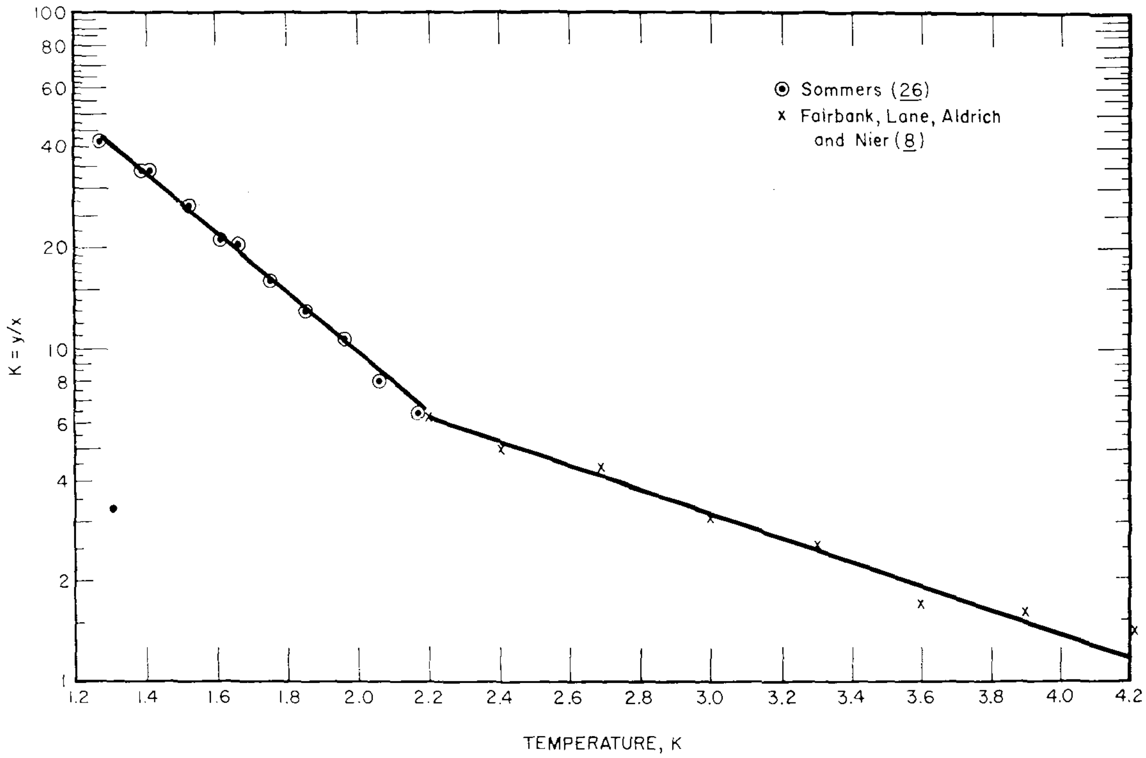

FIGURE A-1. - K-value versus temperature.

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