



UNITED STATES  
DEPARTMENT OF THE INTERIOR  
BUREAU OF MINES  
HELIUM ACTIVITY  
HELIUM RESEARCH CENTER  
INTERNAL REPORT

THERMODYNAMIC PROPERTIES OF HELIUM FOR TEMPERATURES BETWEEN 0°  
AND 150° C AND PRESSURES TO 300 ATMOSPHERES GENERATED FROM  
THE PVT DATA ON HELIUM OBTAINED BY MICHELS AND WOUTERS

BY

B. J. Dalton

Robert E. Barieau

BRANCH Fundamental Research  
PROJECT NO. 4335  
DATE October 1965

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THERMODYNAMIC PROPERTIES OF HELIUM FOR TEMPERATURES BETWEEN 0°  
AND 150° C AND PRESSURES TO 300 ATMOSPHERES GENERATED FROM  
THE PVT DATA ON HELIUM OBTAINED BY MICHELS AND WOUTERS

by

B. J. Dalton<sup>1/</sup> and Robert E. Barieau<sup>2/</sup>

ABSTRACT

The isotherms of helium published by Michels and Wouters have been reevaluated for an equation of the form

$$\left(\frac{pv}{p_0 v_0}\right) = PV = \left(\frac{A_0}{T_0}\right)T + \left(\frac{b_1}{T^{1/4}} + \frac{b_2}{T^{3/4}} + \frac{b_3}{T^{5/4}}\right)P + \left(\frac{c_1}{T^{1/4}} + \frac{c_2}{T^{3/4}} + \frac{c_3}{T^{5/4}}\right)P^2$$

where the best values for the seven parameters were taken to be the least squares values.

From our retreatment of Michels and Wouters' data, we generated six isenthalpic curves along with compressibility factors, Joule-Thomson coefficients, relative molal heat capacities, relative molal enthalpies, and molal heat capacities.

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## RESEARCH REPORT

Submitted by: [Name]

Date: [Date]

Advisor: [Name]

Abstract: [Text]

Introduction: [Text]

Experimental: [Text]

Results: [Text]

Discussion: [Text]

Conclusion: [Text]

## INTRODUCTION

The Helium Research Center is presently engaged in a critical examination of all of the PVT data on helium that appear in the literature. The long-range objective is the development of a single equation of state for helium that will allow all of the thermodynamic properties to be calculated and will reproduce all of the data within the accuracy with which the data are known. A preliminary objective is to obtain the best values of second virial coefficients and to develop an equation that will reproduce the best values as a function of temperature.

In a previous article (3)<sup>3/</sup>, we evaluated second and third

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3/ Underlined numbers in parentheses refer to items in the list of references at the end of this report.

---

virial coefficients of helium from the equation

$$(PV)_{\text{corr.}} = A_t + B(T)P + C(T)P^2 \quad (1)$$

We then represented these B's by a temperature function similar to that employed by Keyes (4).

$$B(T) = \frac{b_1}{T^{1/4}} + \frac{b_2}{T^{3/4}} + \frac{b_3}{T^{5/4}} \quad (2)$$

The B's evaluated from equation (2) represented the original B values within 0.2% or better. This was interpreted to mean that

The first part of the document discusses the importance of maintaining accurate records of all transactions. It emphasizes that every entry should be supported by a valid receipt or invoice. This ensures transparency and allows for easy verification of the data.

In the second section, the author outlines the various methods used to collect and analyze the data. This includes both primary and secondary data collection techniques. The primary data was gathered through direct observation and interviews, while secondary data was obtained from existing reports and databases.

The analysis phase involved using statistical software to identify trends and correlations within the data. The results show a clear upward trend in the number of transactions over the period studied. This is likely due to increased market activity and improved infrastructure.

The final part of the document provides a summary of the findings and offers recommendations for future research. It suggests that further studies should focus on the long-term sustainability of the current trends and the impact of external factors on the data.

The data collected over the past year shows a significant increase in the volume of transactions, particularly in the latter half of the period. This growth is consistent with the overall economic expansion and the implementation of new policies aimed at stimulating trade.

It is important to note that while the overall trend is positive, there are still some areas where the data is less consistent. These areas require further investigation to understand the underlying causes and to develop effective strategies to address them.

In conclusion, the study has provided valuable insights into the current state of the market and the factors influencing it. The findings suggest that the market is generally healthy and growing, but it remains vulnerable to external shocks. Continued monitoring and research are essential to ensure long-term stability and success.

equation (2) represented the second virials of helium for the temperature range 0° to 150° C.

We have previously shown (3) that the C's can be represented by the equation

$$C(T) = \frac{c_1}{T^{1/4}} + \frac{c_2}{T^{3/4}} + \frac{c_3}{T^{5/4}} \quad (3)$$

and that C's evaluated from equation (3) are within the limits of about one standard deviation of the original C values. This was interpreted to mean that equation (3) represented third virials within the apparent precision of the original data from which these values were determined.

Therefore, since we had what we considered to be adequate temperature functions for representing second and third virials of helium, we decided to reevaluate all of the original data reported by Michels and Wouters (6). An equation of the form

$$PV = \left(\frac{A_o}{T_o}\right)T + \left(\frac{b_1}{T^{1/4}} + \frac{b_2}{T^{3/4}} + \frac{b_3}{T^{5/4}}\right)P + \left(\frac{c_1}{T^{1/4}} + \frac{c_2}{T^{3/4}} + \frac{c_3}{T^{5/4}}\right)P^2 \quad (4)$$

was applied to the complete set of data where the seven unknowns:  $(A_o/T_o)$ ;  $b_1$ ;  $b_2$ ;  $b_3$ ;  $c_1$ ;  $c_2$ ;  $c_3$  are to be determined. The best values for the parameters appearing in equation (4) were taken to be the least squares values, each observation being assigned unit weight. Our retreatment of the original PVT data reported by Michels and Wouters is given below.





RECALCULATION OF THE ORIGINAL HELIUM ISOTHERMS  
REPORTED BY MICHELS AND WOUTERS

The experimental data as published by Michels and Wouters are given in table 1 of this report, the PV factors being expressed in Amagat units and the pressures in atmospheres [Amagat units are evaluated from the ratio  $p v / p_0 v_0$ , where  $p$  and  $v$  are the pressure and volume, respectively, at the high pressure and at some given temperature and  $p_0$  and  $v_0$  are the corresponding quantities for the same mass of gas at  $0^\circ$  C and 1 atmosphere]. An equation of the form

$$\left(\frac{PV}{p_0 v_0}\right) = PV = \left(\frac{A_0}{T_0}\right)T + \left(\frac{b_1}{T^{1/4}} + \frac{b_2}{T^{3/4}} + \frac{b_3}{T^{5/4}}\right)P + \left(\frac{c_1}{T^{1/4}} + \frac{c_2}{T^{3/4}} + \frac{c_3}{T^{5/4}}\right)P^2 \quad (4)$$

was applied to the complete set of data where the seven unknowns of equation (4) were determined. The best values for the parameters appearing in equation (4), and given in table 2 of this report, were taken to be the least squares values, each observation being assigned unit weight. The deviations given in table 2 are standard deviations. These deviations were determined by expressing each of the constants in terms of the original observations and applying the law for the "Propagation of Errors" (2, 5).

If the data reported by Michels and Wouters contained a systematic error, one would not expect PV to reduce to the reference state of the gas [the reference state is defined to be:  $PV \equiv 1$  at  $0^\circ$  C and  $P = 1$  atmosphere]. For example, suppose the high pressures were too high by some factor, say two. Then PV would reduce to two at





TABLE 1. - Experimental PVT data for helium obtained by Michels and Wouters

Pressure atm	(PV) <sub>exp</sub>	$[(PV)_{exp} - (PV)_{cal}]_{1/}$
	Michels and Wouters Amagat units	HRC Amagat units
	Temp. = 0° C	
9.0948	1.00431	0.000041
11.2729	1.00547	0.000057
14.0727	1.00693	0.000047
17.6397	1.00876	0.000006
21.8017	1.01094	0.000005
26.7198	1.01351	0.000002
31.5272	1.01606	0.000041
35.1200	1.01790	0.000007
36.2641	1.01855	0.000060
42.6534	1.02183	0.000013
52.3285	1.02685	0.000008
64.2578	1.03303	0.000014
78.6351	1.04045	0.000023
98.010	1.05032	-0.000040
121.759	1.06245	-0.000003
152.160	1.07775	-0.000047
189.813	1.09665	0.000057
	Temp. = 25° C	
9.9266	1.09616	0.000039
12.3036	1.09740	0.000045
15.3591	1.09898	0.000040
19.2526	1.10100	0.000042
23.7946	1.10335	0.000040
29.1618	1.10614	0.000056
34.4061	1.10884	0.000049
38.3280	1.11088	0.000067
39.5749	1.11154	0.000084
46.5446	1.11505	0.000008
57.0978	1.12044	-0.000019
70.1080	1.12708	-0.000035
85.7848	1.13505	-0.000053
106.923	1.14584	0.000023
132.802	1.15881	-0.000037
165.938	1.17533	-0.000059
206.963	1.19573	0.000079

$1/$  (PV)<sub>cal.</sub> was evaluated from equation (4), using the least squares values for the constants given in table 2 of this report.



TABLE 1. - Experimental PVT data for helium obtained by Michels and Wouters (Con.)

Pressure atm	(PV) <sub>exp</sub> Michels and Wouters Amagat units	$\left[ (PV)_{exp} - (PV)_{cal.} \right]_{1/}$ HRC Amagat units
	Temp. = 50° C	
10.7582	1.18799	0.000019
13.3340	1.18930	0.000006
16.6452	1.19100	0.000007
20.8640	1.19315	-0.000006
25.7858	1.19568	0.000003
31.6005	1.19864	-0.000010
37.2837	1.20158	0.000028
41.5319	1.20374	0.000022
42.8832	1.20446	0.000053
50.4317	1.20817	-0.000079
61.8667	1.21402	-0.000034
75.9532	1.22105	-0.000132
92.9345	1.22965	-0.000089
115.820	1.24118	-0.000031
143.833	1.25507	-0.000087
179.686	1.27271	-0.000143
224.074	1.29459	0.000066
Temp. = 75° C		
11.5902	1.27986	0.000042
14.3650	1.28126	0.000030
17.9319	1.28307	0.000028
22.4766	1.28537	0.000021
27.7776	1.28804	0.000003
34.0412	1.29122	0.000012
40.1626	1.29436	0.000058
44.7368	1.29663	0.000019
46.1926	1.29741	0.000065
54.3225	1.30138	-0.000060
66.6350	1.30759	-0.000036
81.8034	1.31510	-0.000121
100.084	1.32425	-0.000083
124.722	1.33658	0.000033
154.876	1.35143	0.000041
193.458	1.37025	0.000043
241.128	1.39312	-0.000073

1/ (PV)<sub>cal</sub> was evaluated from equation (4), using the least squares values for the constants given in table 2 of this report.



TABLE 1. - Experimental PVT data for helium obtained by Michels and Wouters (Con.)

Pressure atm	(PV) <sub>exp</sub> Michels and Wouters Amagat units	$\left[ (PV)_{\text{exp}} - (PV)_{\text{cal.}} \right] \frac{1}{\text{HRC}}$ Amagat units
Temp. = 100° C		
12.4218	1.37170	0.000037
15.3958	1.37320	0.000038
19.2184	1.37512	0.000034
24.0889	1.37757	0.000034
29.7694	1.38040	0.000011
36.4817	1.38379	0.000035
43.0393	1.38707	0.000032
47.9414	1.38951	0.000022
49.4995	1.39029	0.000023
58.2133	1.39459	-0.000023
71.4029	1.40115	-0.000024
87.6561	1.40919	-0.000038
107.240	1.41893	0.000044
133.625	1.43199	0.000168
165.899	1.44761	0.000087
207.183	1.46747	0.000058
258.187	1.49168	-0.000001
Temp. = 125° C		
13.2532	1.46350	-0.000004
16.4261	1.46510	0.000010
20.5043	1.46713	0.000004
25.7004	1.46973	0.000014
31.7595	1.47268	-0.000053
38.9193	1.47625	-0.000041
45.9135	1.47970	-0.000061
51.1443	1.48234	-0.000011
52.8042	1.48311	-0.000063
62.0999	1.48770	-0.000066
76.1779	1.49485	0.000150
93.5026	1.50318	-0.000018
114.390	1.51354	0.000149
142.512	1.52723	0.000205
176.899	1.54360	0.000044
220.871	1.56442	-0.000049
275.189	1.58991	-0.000043

$\frac{1}{\text{HRC}}$  (PV)<sub>cal.</sub> was evaluated from equation (4), using the least squares values for the constants given in table 2 of this report.







TABLE 1. - Experimental PVT data for helium obtained by Michels and Wouters (Con.)

Pressure atm	(PV) <sub>exp</sub> Michels and Wouters Amagat units	$\left[ (PV)_{exp} - (PV)_{cal.} \right] \frac{1}{HRC}$ Amagat units
	Temp. = 150° C	
14.0847	1.55532	-0.000023
17.4566	1.55701	-0.000004
21.7902	1.55914	-0.000020
27.3116	1.56187	-0.000020
33.7509	1.56502	-0.000049
41.3568	1.56871	-0.000107
48.7883	1.57235	-0.000121
54.3454	1.57512	-0.000079
56.1089	1.57593	-0.000133
65.9811	1.58068	-0.000216
80.9284	1.58807	-0.000119
99.3435	1.59708	-0.000051
121.520	1.60787	0.000030
151.375	1.62221	0.000058
187.909	1.63967	0.000169
234.562	1.66139	-0.000005
292.153	1.68792	-0.000095

1/ (PV)<sub>cal.</sub> was evaluated from equation (4), using the least squares values for the constants given in table 2 of this report.



TABLE 2. - Virial coefficients of helium as evaluated by the Helium Research Center from the original PVT data obtained by Michels and Wouters: 0° C = 273.15° K

$$\begin{aligned} (A_o/T_o) &= (0.36590932 \pm 0.00000411) \times 10^{-2} \\ b_1 &= (3.21079494 \pm 0.16219855) \times 10^{-3} \\ b_2 &= -(2.76069068 \pm 0.60075141) \times 10^{-2} \\ b_3 &= (1.64599720 \pm 0.55397920) \times 10^{-1} \\ A_o &= 0.99948130 \pm 0.00001122 \\ c_1 &= -(3.47366275 \pm 0.89251908) \times 10^{-6} \\ c_2 &= (1.19284347 \pm 0.33335061) \times 10^{-4} \\ c_3 &= -(1.11341304 \pm 0.31003730) \times 10^{-3} \end{aligned}$$

t, ° C	$A_t$ <sup>1/</sup>	$(B \cdot 10^3)$ <sup>2/</sup>	$(-C \cdot 10^7)$ <sup>3/</sup>
0	0.999481 ± 0.000011	0.52714 ± 0.00061	0.8177 ± 0.0377
25	1.090959 ± 0.000012	0.52078 ± 0.00042	0.7216 ± 0.0226
50	1.182436 ± 0.000013	0.51521 ± 0.00041	0.6688 ± 0.0195
75	1.273913 ± 0.000014	0.51024 ± 0.00040	0.6455 ± 0.0182
100	1.365391 ± 0.000015	0.50573 ± 0.00038	0.6426 ± 0.0158
125	1.456868 ± 0.000016	0.50161 ± 0.00038	0.6538 ± 0.0143
150	1.548345 ± 0.000017	0.49779 ± 0.00045	0.6750 ± 0.0176

<sup>1/</sup>  $A_t = (A_o/T_o)T$ , where  $T = (273.15 + t, ° C)$ .

<sup>2/</sup> Evaluated from equation (2), using the least squares values for  $b_1$ ,  $b_2$ , and  $b_3$  given above.

<sup>3/</sup> Evaluated from equation (3), using the least squares values for  $c_1$ ,  $c_2$ , and  $c_3$  given above.



$P = 1$  atm. and  $0^\circ$  C. Therefore, whether or not our function, equation (4), reduces to the reference state of the gas can be used to test for the presence of a systematic error.

We carry out this test for a systematic error in the following way. We evaluate the unknowns of equation (4) by least squares methods. We then evaluate our function, equation (4), at  $T = 273.15^\circ$  K and  $P = 1$  atm. and compare this value to one. If the PV product is different from one, a statistical test is carried out to see if this difference is significant. If this difference is of statistical significance, then this value represents the systematic error which is removed by multiplying all of the published PV's by the appropriate factor to remove it.

Suppose we evaluate the right-hand side of equation (4) at  $0^\circ$  C and  $P = 1$  atm. From the data given in table 2, we have

$$A_{0^\circ} = \left(\frac{A_0}{T_0}\right)T_0 = 0.99948130 \pm 0.00001122, \text{ Amagat units}$$

$$B_{0^\circ} = \left(\frac{b_1}{T_0^{1/4}} + \frac{b_2}{T_0^{3/4}} + \frac{b_3}{T_0^{5/4}}\right) = (0.52714 \pm 0.00061) \times 10^{-3}$$

$$C_{0^\circ} = \left(\frac{c_1}{T_0^{1/4}} + \frac{c_2}{T_0^{3/4}} + \frac{c_3}{T_0^{5/4}}\right) = - (0.8177 \pm 0.0377) \times 10^{-7}$$

where  $T_0 = 273.15^\circ$  K. Therefore,

$$\begin{array}{l} \text{PV} \\ | \\ 0^\circ \text{ C} \\ | \\ P=1 \text{ atm.} \end{array} = A_{0^\circ} + B_{0^\circ} + C_{0^\circ} = 1.00000836$$





Since PV is not exactly equal to one, this indicates that there might be a systematic error in the data. Now in order to decide if this difference is statistically significant, we need to have an estimate of the standard error of PV at 0° C and P = 1 atm. We evaluated the standard error of our function, equation (4), at 0° C and P = 1 atm. by expressing  $A_{0^{\circ}}$ ,  $B_{0^{\circ}}$ , and  $C_{0^{\circ}}$  in terms of the original data and applying the law for the "Propagation of Errors" (2, 5). When we did this, we got

$$S_{(PV)} \left| \begin{array}{l} 0^{\circ} \text{ C} \\ P=1 \text{ atm.} \end{array} \right. = \pm 0.00001095$$

or

$$PV \left| \begin{array}{l} 0^{\circ} \text{ C} \\ P=1 \text{ atm.} \end{array} \right. = 1.000008 \pm 0.000011, \text{ Amagat units}$$

We see that the difference between the reference state of the gas and the PV product evaluated from equation (4) is less than a standard deviation. This is taken as statistical evidence that there is no systematic error in the experimental data reported by Michels and Wouters.

We have previously shown (3) that the temperatures as given by the primary temperature scale have smaller uncertainties than those evaluated from the PV measurements. We concluded, therefore, that





the primary scale was more accurate and that the temperature of each isotherm is as given by the primary scale. This means that we should set  $A = RT$  for each isotherm, where  $T$  is evaluated from the primary temperature scale.

We reevaluated the PVT data given in reference 6 in the following way: from equation (4), for  $T = T_o = 273.15^\circ \text{ K}$  and  $P = 1 \text{ atm.}$ , we have

$$PV \cong 1 = \frac{A_{0^\circ}}{T_o} T_o + \left( \frac{b_1}{T_o^{1/4}} + \frac{b_2}{T_o^{3/4}} + \frac{b_3}{T_o^{5/4}} \right) + \left( \frac{c_1}{T_o^{1/4}} + \frac{c_2}{T_o^{3/4}} + \frac{c_3}{T_o^{5/4}} \right) \quad (5)$$

or,

$$A_{0^\circ} = 1 - \left( \frac{b_1}{T_o^{1/4}} + \frac{b_2}{T_o^{3/4}} + \frac{b_3}{T_o^{5/4}} \right) - \left( \frac{c_1}{T_o^{1/4}} + \frac{c_2}{T_o^{3/4}} + \frac{c_3}{T_o^{5/4}} \right) \quad (6)$$

Substituting equation (6) into equation (4), we get

$$PV = \left[ \begin{aligned} & \frac{T}{T_o} + b_1 \left( \frac{P}{T^{1/4}} - \frac{T}{T_o^{5/4}} \right) + b_2 \left( \frac{P}{T^{3/4}} - \frac{T}{T_o^{7/4}} \right) \\ & + b_3 \left( \frac{P}{T^{5/4}} - \frac{T}{T_o^{9/4}} \right) + c_1 \left( \frac{P^2}{T^{1/4}} - \frac{T}{T_o^{5/4}} \right) \\ & + c_2 \left( \frac{P^2}{T^{3/4}} - \frac{T}{T_o^{7/4}} \right) + c_3 \left( \frac{P^2}{T^{5/4}} - \frac{T}{T_o^{9/4}} \right) \end{aligned} \right] \quad (7)$$

Equation (7) was then applied to the complete set of data to give the residuals given in column 3 of table 3. The parameters appearing in equation (7) were evaluated by least squares solution,



TABLE 3. - Experimental compressibility data for helium as reevaluated using equations (6) and (7):  
PV  $\equiv$  1 at P = 1 atm. and 0° C

Pressure atm	(PV) <sub>exp</sub>	[(PV) <sub>exp</sub> - (PV) <sub>cal.</sub> ] HRC Amagat units
	Michels and Wouters Amagat units	
Temp. = 0° C		
9.0948	1.00431	0.000048
11.2729	1.00547	0.000063
14.0727	1.00693	0.000052
17.6397	1.00876	0.000011
21.8017	1.01094	0.000010
26.7198	1.01351	0.000006
31.5272	1.01606	0.000044
35.1200	1.01790	0.000009
36.2641	1.01855	0.000062
42.6534	1.02183	0.000015
52.3285	1.02685	0.000008
64.2578	1.03303	0.000013
78.6351	1.04045	0.000021
98.010	1.05032	-0.000043
121.759	1.06245	-0.000006
152.160	1.07775	-0.000049
189.813	1.09665	0.000060
Temp. = 25° C		
9.9266	1.09616	0.000046
12.3036	1.09740	0.000052
15.3591	1.09898	0.000046
19.2526	1.10100	0.000047
23.7946	1.10335	0.000045
29.1618	1.10614	0.000059
34.4061	1.10884	0.000051
38.3280	1.11088	0.000069
39.5749	1.11154	0.000086
46.5446	1.11505	0.000009
57.0978	1.12044	-0.000019
70.1080	1.12708	-0.000037
85.7848	1.13505	-0.000056
106.923	1.14584	0.000019
132.802	1.15881	-0.000041
165.938	1.17533	-0.000061
206.963	1.19573	0.000083



TABLE 3. - Experimental compressibility data for helium as reevaluated using equations (6) and (7):  
PV  $\equiv$  1 at P = 1 atm. and 0° C (Con.)

Pressure atm	(PV) <sub>exp</sub>	$[(PV)_{exp} - (PV)_{cal.}]$
	Michels and Wouters Amagat units	HRC Amagat units
Temp. = 50° C		
10.7582	1.18799	0.000027
13.3340	1.18930	0.000013
16.6452	1.19100	0.000013
20.8640	1.19315	0.000000
25.7858	1.19568	0.000008
31.6005	1.19864	-0.000006
37.2837	1.20158	0.000031
41.5319	1.20374	0.000024
42.8832	1.20446	0.000055
50.4317	1.20817	-0.000078
61.8667	1.21402	-0.000035
75.9532	1.22105	-0.000134
92.9345	1.22965	-0.000093
115.820	1.24118	-0.000035
143.833	1.25507	-0.000091
179.686	1.27271	-0.000145
224.074	1.29459	0.000071
Temp. = 75° C		
11.5902	1.27986	0.000050
14.3650	1.28126	0.000038
17.9319	1.28307	0.000035
22.4766	1.28537	0.000027
27.7776	1.28804	0.000008
34.0412	1.29122	0.000016
40.1626	1.29436	0.000061
44.7368	1.29663	0.000022
46.1926	1.29741	0.000067
54.3225	1.30138	-0.000059
66.6350	1.30759	-0.000037
81.8034	1.31510	-0.000123
100.084	1.32425	-0.000087
124.722	1.33658	0.000028
154.876	1.35143	0.000037
193.458	1.37025	0.000041
241.128	1.39312	-0.000068







TABLE 3. - Experimental compressibility data for helium as reevaluated using equations (6) and (7):  
PV  $\equiv$  1 at P = 1 atm. and 0° C (Con.)

Pressure atm	(PV) <sub>exp</sub>	$[(PV)_{exp} - (PV)_{cal.}]$
	Michels and Wouters Amagat units	HRC Amagat units
	Temp. = 100° C	
12.4218	1.37170	0.000046
15.3958	1.37320	0.000047
19.2184	1.37512	0.000041
24.0889	1.37757	0.000041
29.7694	1.38040	0.000016
36.4817	1.38379	0.000039
43.0393	1.38707	0.000035
47.9414	1.38951	0.000024
49.4995	1.39029	0.000025
58.2133	1.39459	-0.000022
71.4029	1.40115	-0.000025
87.6561	1.40919	-0.000040
107.240	1.41893	0.000039
133.625	1.43199	0.000163
165.899	1.44761	0.000082
207.183	1.46747	0.000056
258.187	1.49168	0.000004
	Temp. = 125° C	
13.2532	1.46350	0.000005
16.4261	1.46510	0.000019
20.5043	1.46713	0.000012
25.7004	1.46973	0.000021
31.7595	1.47268	-0.000047
38.9193	1.47625	-0.000037
45.9135	1.47970	-0.000057
51.1443	1.48234	-0.000009
52.8042	1.48311	-0.000060
62.0999	1.48770	-0.000065
76.1779	1.49485	0.000149
93.5026	1.50318	-0.000021
114.390	1.51354	0.000144
142.512	1.52723	0.000200
176.899	1.54360	0.000039
220.871	1.56442	-0.000051
275.189	1.58991	-0.000038



TABLE 3. - Experimental compressibility data for helium as reevaluated using equations (6) and (7):  
PV  $\equiv$  1 at P = 1 atm. and 0° C (Con.)

Pressure atm	(PV) <sub>exp</sub>	$[(PV)_{exp} - (PV)_{cal.}]$
	Michels and Wouters Amagat units	HRC Amagat units
	Temp. = 150° C	
14.0847	1.55532	-0.000013
17.4566	1.55701	0.000005
21.7902	1.55914	-0.000012
27.3116	1.56187	-0.000013
33.7509	1.56502	-0.000043
41.3568	1.56871	-0.000102
48.7883	1.57235	-0.000117
54.3454	1.57512	-0.000076
56.1089	1.57593	-0.000131
65.9811	1.58068	-0.000215
80.9284	1.58807	-0.000120
99.3435	1.59708	-0.000054
121.520	1.60787	0.000025
151.375	1.62221	0.000053
187.909	1.63967	0.000163
234.562	1.66139	-0.000007
292.153	1.68792	-0.000090



each observation being given unit weight. These constants are given in table 4 of this report. The deviations given in table 4 are standard deviations. These deviations were evaluated by expressing each of the constants in terms of the original observations and applying the law for the "Propagation of Errors" (2, 5).

From our reevaluation of Michels and Wouters' data, we evaluated thermodynamic properties of helium for temperatures between 0° and 150° C and pressures to 300 atmospheres. Our calculations and the quantities we evaluated are given in the next section.

#### THERMODYNAMIC PROPERTIES OF HELIUM AS EVALUATED FROM THE RESULTS OF MICHELS AND WOUTERS' WORK

We generated six isenthalpic curves from the results of our recalculation of Michels and Wouters' PVT data on helium, corresponding to the isenthalpic zero pressure-temperature intercepts reported by Barieau and Briggs (1) in their reevaluation of Roebuck and Osterberg's Joule-Thomson data for helium. We generated these isenthalpic curves from Michels and Wouters' data in the following way. The helium isotherms reported in reference 6 were represented by the equation

$$PV = \left(\frac{A_{0^{\circ}}}{T_o}\right)T + \left(\frac{b_1}{T^{1/4}} + \frac{b_2}{T^{3/4}} + \frac{b_3}{T^{5/4}}\right)P + \left(\frac{c_1}{T^{1/4}} + \frac{c_2}{T^{3/4}} + \frac{c_3}{T^{5/4}}\right)P^2 \quad (8)$$

where  $A_{0^{\circ}}$  is defined by equation (6) and the b's and c's are the least squares values previously determined from equation (7).





TABLE 4. - Virial coefficients for helium as calculated from equations (6) and (7)

$$\begin{aligned}
 b_1 &= (3.20923530 \pm 0.16188694) \times 10^{-3} \\
 b_2 &= -(2.74977122 \pm 0.59947520) \times 10^{-2} \\
 b_3 &= (1.63456005 \pm 0.55275691) \times 10^{-1} \\
 c_1 &= -(3.45274355 \pm 0.89045538) \times 10^{-6} \\
 c_2 &= (1.18441022 \pm 0.33255397) \times 10^{-4} \\
 c_3 &= -(1.10625748 \pm 0.30932473) \times 10^{-3}
 \end{aligned}$$

$$A_{0^\circ\text{C}} \Big|_{P=1 \text{ atm.}} = 1 - \frac{b_1}{T_0^{1/4}} - \frac{b_2}{T_0^{3/4}} - \frac{b_3}{T_0^{5/4}} - \frac{c_1}{T_0^{1/4}} - \frac{c_2}{T_0^{3/4}} - \frac{c_3}{T_0^{5/4}}$$

t, °C	$A_t = A_{0^\circ} \left( \frac{T}{T_0} \right)$	$(B \times 10^3)^{1/}$	$-(C \times 10^7)^{2/}$
0	0.999473	$0.52735 \pm 0.00054$	$0.8273 \pm 0.0354$
25	1.090949	$0.52101 \pm 0.00031$	$0.7310 \pm 0.0189$
50	1.182426	$0.51544 \pm 0.00028$	$0.6778 \pm 0.0154$
75	1.273902	$0.51047 \pm 0.00026$	$0.6541 \pm 0.0142$
100	1.365379	$0.50597 \pm 0.00022$	$0.6507 \pm 0.0117$
125	1.456855	$0.50184 \pm 0.00022$	$0.6614 \pm 0.0104$
150	1.548332	$0.49802 \pm 0.00033$	$0.6820 \pm 0.0150$

$$\underline{1/} \quad B(T) = \frac{1}{T^{1/4}} \left[ b_1 + \frac{b_2}{T^{1/2}} + \frac{b_3}{T} \right]$$

$$\underline{2/} \quad C(T) = \frac{1}{T^{1/4}} \left[ c_1 + \frac{c_2}{T^{1/2}} + \frac{c_3}{T} \right]$$

Note: The variances and covariances of the parameters appearing in equation (7) are given in the appendix of this report.



Dividing both sides of equation (8) by  $TP$ ,

$$\frac{V}{T} = \left(\frac{A_{0^\circ}}{T_0 P}\right) + \left(\frac{b_1}{T^{5/4}} + \frac{b_2}{T^{7/4}} + \frac{b_3}{T^{9/4}}\right) + \left(\frac{c_1}{T^{5/4}} + \frac{c_2}{T^{7/4}} + \frac{c_3}{T^{9/4}}\right)P \quad (9)$$

Differentiating equation (9) with respect to  $(1/T)$ , keeping the pressure constant, we get

$$\left[\frac{\partial(V/T)}{\partial(1/T)}\right]_P = \frac{1}{4T^{1/4}} \left[ \left(5b_1 + \frac{7b_2}{T^{1/2}} + \frac{9b_3}{T}\right) + \left(5c_1 + \frac{7c_2}{T^{1/2}} + \frac{9c_3}{T}\right)P \right] \quad (10)$$

But

$$\left[\frac{\partial(V/T)}{\partial(1/T)}\right]_P = \left(\frac{\partial H}{\partial P}\right)_T \quad (11)$$

Substituting equation (11) into equation (10), we get

$$\left(\frac{\partial H}{\partial P}\right)_T = \frac{1}{4T^{1/4}} \left[ \left(5b_1 + \frac{7b_2}{T^{1/2}} + \frac{9b_3}{T}\right) + \left(5c_1 + \frac{7c_2}{T^{1/2}} + \frac{9c_3}{T}\right)P \right] \quad (12)$$

Integrating equation (12) from  $P = 0$  to  $P = P$  at constant temperature, we get

$$\left(H_P - H_{P=0}\right)_T = \frac{1}{4T^{1/4}} \left[ \left(5b_1 + \frac{7b_2}{T^{1/2}} + \frac{9b_3}{T}\right)P + \left(5c_1 + \frac{7c_2}{T^{1/2}} + \frac{9c_3}{T}\right) \frac{P^2}{2} \right] \quad (13)$$

We employed equation (13) and the expression

$$(\Delta H)_P = C_P^0 \Delta T = \frac{5}{2} R \Delta T \quad (14)$$



to generate isenthalpic curves for helium from Michels and Wouters' data corresponding to the isenthalpic zero pressure-temperature intercepts reported in reference 1. The isenthalpic zero pressure-temperature intercepts reported by Barieau and Briggs (1) are given in table 5 of this report; the isenthalpic curves we generated from the data of Michels and Wouters, corresponding to the zero pressure-temperature intercepts of table 5, are given in table 6 of this report.

Compressibility factors for helium for temperatures between 0° and 150° C and pressures to 300 atmospheres are given in table 7 of this report. These Z's were evaluated by dividing both sides of equation (8) by the factor  $(A_{0^\circ}/T_0)T$ . When we do this, we see that Z is expressible by the equation

$$\frac{(PV)}{(A_{0^\circ}/T_0)T} = Z = 1 + \frac{1}{(A_{0^\circ}/T_0)} \left[ \left( \frac{b_1}{T^{5/4}} + \frac{b_2}{T^{7/4}} + \frac{b_3}{T^{9/4}} \right) P + \left( \frac{c_1}{T^{5/4}} + \frac{c_2}{T^{7/4}} + \frac{c_3}{T^{9/4}} \right) P^2 \right] \quad (15)$$

The deviations listed in table 7 are standard deviations. These deviations were determined by expressing Z in terms of the original observations and applying the law for the "Propagation of Errors" (2, 5).

Table 8 of this report gives  $\rho R$  products as a function of temperature and pressure, where  $\rho$  is the density and R is the gas constant. These  $\rho R$  products were determined from the equation

$$\rho R = \frac{P}{ZT} \quad (16)$$





TABLE 5. - Isenthalpic zero pressure-temperature intercepts reported by Briggs and Barieau in their recalculation of Roebuck and Osterberg's  $\mu$  data for helium for temperatures between 0° and 150° C

Curve	<u>Zero Pressure-Temperature Intercept</u>	
	° C	° K
150	165.414	438.564
100	113.099	386.249
75	88.214	361.364
50	63.789	336.939
25	36.770	309.920
0	12.141	285.291

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TABLE 6. - Isoenthalpic curves generated from the PVT data on helium obtained by Michels and Wouters

<u>T</u> <u>°K</u>	<u>P</u> <u>atm</u>	<u>T</u> <u>°K</u>	<u>P</u> <u>atm</u>	<u>T</u> <u>°K</u>	<u>P</u> <u>atm</u>
438.564	0.0000	386.249	0.0000	361.364	0.0000
438	9.2506	386	4.0150	361	5.8132
437	25.6527	385	20.1462	360	21.7957
436	42.0560	384	36.2888	359	37.7973
435	58.4609	383	52.4438	358	53.8193
434	74.8678	382	68.6122	357	69.8631
433	91.2774	381	84.7951	356	85.9301
432	107.6903	380	100.9934	355	102.0217
431	124.1069	379	117.2084	354	118.1395
430	140.5279	378	133.4411	353	134.2850
429	156.9539	377	149.6927	352	150.4599
428	173.3854	376	165.9644	351	166.6659
427	189.8233	375	182.2575	350	182.9046
426	206.2681	374	198.5733	349	199.1780
425	222.7204	373	214.9131	348	215.4878
424	239.1811	372	231.2783	347	231.8361
423	255.6508	371	247.6704	346	248.2249
422	272.1303	370	264.0907	345	264.6563
421	288.6203	369	280.5409	344	281.1324
420	305.1217	368	297.0224	343	297.6557



TABLE 6. - Isenthalpic curves generated from the PVT data on helium obtained by Michels and Wouters (Con.)

<u>T</u> <u>°K</u>	<u>P</u> <u>atm</u>	<u>T</u> <u>°K</u>	<u>P</u> <u>atm</u>	<u>T</u> <u>°K</u>	<u>P</u> <u>atm</u>
336.939	0.0000	309.920	0.0000	285.291	0.0000
336	14.8420	309	14.3429	285	4.4646
335	30.6751	308	29.9722	284	19.8419
334	46.5379	307	45.6449	283	35.2764
333	62.4320	306	61.3635	282	50.7715
332	78.3594	305	77.1307	281	66.3309
331	94.3221	304	92.9493	280	81.9584
330	110.3221	303	108.8224	279	97.6582
329	126.3616	302	124.7530	278	113.4345
328	142.4427	301	140.7444	277	129.2919
327	158.5679	300	156.8001	276	145.2353
326	174.7395	299	172.9234	275	161.2697
325	190.9600	298	189.1184	274	177.4005
324	207.2321	297	205.3889	273	193.6335
323	223.5585	296	221.7390	272	209.9747
322	239.9421	295	238.1732	271	226.4307
321	256.3858	294	254.6961	270	243.0083
320	272.8927	293	271.3126	269	259.7150
319	289.4662	292	288.0278	268	276.5585
318	306.1096	291	304.8472	267	293.5472



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TABLE 7. - Compressibility factors of helium:  $Z = P/\rho RT$

<u>T, ° K</u>	<u>P,atm.</u> <u>0</u>	<u>P,atm.</u> <u>1</u>	<u>P,atm.</u> <u>5</u>
273.15	1.0000000	1.0005275 ± 0.0000005	1.0026361 ± 0.0000026
275	1.0000000	1.0005235 ± 0.0000005	1.0026159 ± 0.0000025
300	1.0000000	1.0004742 ± 0.0000003	1.0023695 ± 0.0000013
325	1.0000000	1.0004331 ± 0.0000002	1.0021641 ± 0.0000011
350	1.0000000	1.0003983 ± 0.0000002	1.0019903 ± 0.0000010
375	1.0000000	1.0003685 ± 0.0000002	1.0018414 ± 0.0000008
400	1.0000000	1.0003426 ± 0.0000002	1.0017122 ± 0.0000008
425	1.0000000	1.0003200 ± 0.0000002	1.0015993 ± 0.0000011



TABLE 7. - Compressibility factors of helium:  $Z = P/\rho RT$  (Con.)

<u>T, ° K</u>	P,atm.		P,atm.		P,atm.	
	<u>10</u>		<u>20</u>		<u>50</u>	
273.15	1.0052680	$\pm 0.0000051$	1.0105194	$\pm 0.0000095$	1.0261744	$\pm 0.0000190$
275	1.0052277	$\pm 0.0000048$	1.0104390	$\pm 0.0000089$	1.0259756	$\pm 0.0000178$
300	1.0047357	$\pm 0.0000026$	1.0094581	$\pm 0.0000048$	1.0235462	$\pm 0.0000098$
325	1.0043254	$\pm 0.0000022$	1.0086395	$\pm 0.0000042$	1.0215137	$\pm 0.0000088$
350	1.0039781	$\pm 0.0000019$	1.0079461	$\pm 0.0000036$	1.0197887	$\pm 0.0000076$
375	1.0036804	$\pm 0.0000015$	1.0073512	$\pm 0.0000028$	1.0183069	$\pm 0.0000060$
400	1.0034222	$\pm 0.0000015$	1.0068354	$\pm 0.0000028$	1.0170206	$\pm 0.0000060$
425	1.0031964	$\pm 0.0000021$	1.0063839	$\pm 0.0000040$	1.0158939	$\pm 0.0000086$

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TABLE 7. - Compressibility factors of helium:  $Z = P/\rho RT$  (Con.)

<u>T, ° K</u>	P,atm.	P,atm.	P,atm.
	<u>75</u>	<u>100</u>	<u>150</u>
273.15	1.0391064 ± 0.0000229	1.0519349 ± 0.0000242	1.0772815 ± 0.0000285
275	1.0388110 ± 0.0000215	1.0515446 ± 0.0000227	1.0767070 ± 0.0000267
300	1.0351953 ± 0.0000121	1.0467618 ± 0.0000129	1.0696468 ± 0.0000142
325	1.0321641 ± 0.0000111	1.0427435 ± 0.0000122	1.0636893 ± 0.0000130
350	1.0295874 ± 0.0000096	1.0393224 ± 0.0000107	1.0586010 ± 0.0000114
375	1.0273713 ± 0.0000076	1.0363765 ± 0.0000086	1.0542089 ± 0.0000092
400	1.0254460 ± 0.0000079	1.0338148 ± 0.0000090	1.0503826 ± 0.0000098
425	1.0237584 ± 0.0000113	1.0315679 ± 0.0000129	1.0470221 ± 0.0000141





TABLE 7. - Compressibility factors of helium:  $Z = P/\rho RT$  (Con.)

<u>T, ° K</u>	<u>P,atm. 200</u>	<u>P,atm. 250</u>	<u>P,atm. 300</u>
273.15	1.1022142 ± 0.0000554	1.1267331 ± 0.0001061	1.1508381 ± 0.0001765
275	1.1014628 ± 0.0000520	1.1258120 ± 0.0000998	1.1497545 ± 0.0001662
300	1.0922011 ± 0.0000247	1.1144249 ± 0.0000471	1.1363180 ± 0.0000793
325	1.0843513 ± 0.0000183	1.1047295 ± 0.0000332	1.1248237 ± 0.0000563
350	1.0776246 ± 0.0000158	1.0963932 ± 0.0000282	1.1149067 ± 0.0000476
375	1.0718041 ± 0.0000122	1.0891620 ± 0.0000211	1.1062827 ± 0.0000356
400	1.0667241 ± 0.0000109	1.0828392 ± 0.0000163	1.0987280 ± 0.0000271
425	1.0622564 ± 0.0000154	1.0772708 ± 0.0000224	1.0920654 ± 0.0000370



TABLE 8. - Values of  $\rho R$ , atm/° K

<u>T, ° K</u>	<u>P, atm.</u> <u>0</u>	<u>P, atm.</u> <u>1</u>	<u>P, atm.</u> <u>5</u>	<u>P, atm.</u> <u>10</u>
273.15	0	0.00365906	0.01825683	0.03641807
275	0	0.00363446	0.01813438	0.03617453
300	0	0.00333175	0.01662727	0.03317622
325	0	0.00307559	0.01535139	0.03063671
350	0	0.00285601	0.01425734	0.02845822
375	0	0.00266568	0.01330883	0.02656888
400	0	0.00249914	0.01247863	0.02491474
425	0	0.00235219	0.01174592	0.02345444



TABLE 8. - Values of  $\rho R$ , atm/ $^{\circ}$  K (Con.)

<u>T, <math>^{\circ}</math> K</u>	<u>P, atm. 20</u>	<u>P, atm. 50</u>	<u>P, atm. 75</u>	<u>P, atm. 100</u>
273.15	0.07245763	0.17838061	0.26424091	0.34802460
275	0.07197591	0.17721491	0.26253792	0.34581163
300	0.06604203	0.16283258	0.24150032	0.31844240
325	0.06101135	0.15060606	0.22357805	0.29507959
350	0.05669237	0.14008504	0.20812775	0.27490439
375	0.05294413	0.13093630	0.19467158	0.25730675
400	0.04966055	0.12290803	0.18284727	0.24182281
425	0.04676031	0.11580645	0.17237523	0.22809368





TABLE 8. - Values of  $\rho R$ , atm/ $^{\circ}$  K (Con.)

<u>T, <math>^{\circ}</math> K</u>	<u>P, atm.</u> <u>150</u>	<u>P, atm.</u> <u>200</u>	<u>P, atm.</u> <u>250</u>	<u>P, atm.</u> <u>300</u>
273.15	0.50975425	0.66429774	0.81230242	0.95434591
275	0.50659513	0.66027896	0.80749799	0.94881913
300	0.46744404	0.61038819	0.74776985	0.88003530
325	0.43390343	0.56751404	0.69630693	0.82064145
350	0.40484698	0.53026681	0.65148682	0.76880230
375	0.37943144	0.49760339	0.61209138	0.72314248
400	0.35701276	0.46872476	0.57718634	0.68260755
425	0.33709049	0.44300816	0.54604216	0.64637368



where  $P$  is the pressure in atmospheres,  $T$  is the temperature in  $^{\circ}K$ , and  $Z$  is the compressibility factor of helium corresponding to a given  $P$  and  $T$ .

If we divide both sides of equation (13) by  $R$ , where  $R = (A_{0^{\circ}}/T_0)$ , then we get an expression from which we can evaluate relative enthalpies,  $L/R$ . That is,

$$\left(\frac{H_P - H_{P=0}}{R}\right)_T = \left(\frac{L}{R}\right)_T = \frac{1}{4(A_{0^{\circ}}/T_0)T^{1/4}} \left[ \begin{aligned} &\left(5b_1 + \frac{7b_2}{T^{1/2}} + \frac{9b_3}{T}\right)P \\ &+ \left(5c_1 + \frac{7c_2}{T^{1/2}} + \frac{9c_3}{T}\right)\frac{P^2}{2} \end{aligned} \right] \quad (17)$$

Relative enthalpies are given in table 9 of this report for temperatures between  $0^{\circ}$  and  $150^{\circ}C$  and pressures to 300 atmospheres along with the standard deviation of each of these values.

If we differentiate equation (17) with regard to the temperature, keeping the pressure constant, we get an expression of the form

$$\frac{\left[ \frac{d(H_P - H_{P=0})}{dT} \right]_P}{R} = \left( \frac{C_P - C_P^0}{R} \right) = - \frac{1}{16(A_{0^{\circ}}/T_0)T^{5/4}} \left[ \begin{aligned} &\left(5b_1 + \frac{21b_2}{T^{1/2}} + \frac{45b_3}{T}\right)P \\ &+ \left(5c_1 + \frac{21c_2}{T^{1/2}} + \frac{45c_3}{T}\right)\frac{P^2}{2} \end{aligned} \right] \quad (18)$$



TABLE 9. - Values of relative enthalpies,  $\frac{H_P - H_{P=0}}{R} = \frac{L}{R}$ , ° K

<u>T, ° K</u>	<u>P, atm.</u> <u>0</u>	<u>P, atm.</u> <u>1</u>	<u>P, atm.</u> <u>5</u>	<u>P, atm.</u> <u>10</u>
273.15	0	0.164 ± 0.002	0.822 ± 0.008	1.642 ± 0.016
275	0	0.164 ± 0.002	0.820 ± 0.008	1.639 ± 0.015
300	0	0.161 ± 0.001	0.807 ± 0.004	1.613 ± 0.008
325	0	0.159 ± 0.000	0.796 ± 0.002	1.591 ± 0.004
350	0	0.157 ± 0.000	0.786 ± 0.002	1.572 ± 0.004
375	0	0.156 ± 0.001	0.778 ± 0.003	1.556 ± 0.006
400	0	0.154 ± 0.001	0.771 ± 0.004	1.542 ± 0.007
425	0	0.153 ± 0.001	0.765 ± 0.004	1.530 ± 0.009





TABLE 9. - Values of relative enthalpies,  $\frac{H_P - H_{P=0}}{R} = \frac{L}{R}, \text{ }^\circ \text{K}$  (Con.)

<u>T, ° K</u>	<u>P,atm. 20</u>	<u>P,atm. 50</u>	<u>P,atm. 75</u>	<u>P,atm. 100</u>
273.15	3.277 ± 0.031	8.148 ± 0.070	12.166 ± 0.097	16.147 ± 0.118
275	3.273 ± 0.030	8.139 ± 0.067	12.153 ± 0.093	16.132 ± 0.114
300	3.221 ± 0.016	8.021 ± 0.037	11.992 ± 0.051	15.937 ± 0.062
325	3.179 ± 0.008	7.923 ± 0.019	11.856 ± 0.026	15.770 ± 0.032
350	3.142 ± 0.008	7.839 ± 0.018	11.739 ± 0.025	15.624 ± 0.031
375	3.111 ± 0.011	7.766 ± 0.025	11.635 ± 0.036	15.494 ± 0.044
400	3.084 ± 0.014	7.702 ± 0.033	11.542 ± 0.046	15.376 ± 0.057
425	3.060 ± 0.017	7.643 ± 0.039	11.459 ± 0.054	15.269 ± 0.067



TABLE 9. - Values of relative enthalpies,  $\frac{H_P - H_{P=0}}{R} = \frac{L}{R}$ , ° K (Con.)

<u>T, ° K</u>	<u>P,atm. 150</u>	<u>P,atm. 200</u>	<u>P,atm. 250</u>	<u>P,atm. 300</u>
273.15	23.997 ± 0.147	31.698 ± 0.161	39.250 ± 0.168	46.653 ± 0.184
275	23.979 ± 0.141	31.681 ± 0.154	39.237 ± 0.161	46.647 ± 0.177
300	23.746 ± 0.076	31.449 ± 0.082	39.047 ± 0.085	46.537 ± 0.095
325	23.540 ± 0.038	31.233 ± 0.041	38.849 ± 0.042	46.388 ± 0.048
350	23.353 ± 0.039	31.028 ± 0.044	38.647 ± 0.046	46.211 ± 0.048
375	23.183 ± 0.057	30.833 ± 0.065	38.444 ± 0.068	46.016 ± 0.070
400	23.025 ± 0.073	30.646 ± 0.083	38.241 ± 0.087	45.809 ± 0.090
425	22.877 ± 0.086	30.467 ± 0.096	38.039 ± 0.101	45.593 ± 0.105

No.	Name	Age	Sex	Profession	Religion
1	...	...	...	...	...
2	...	...	...	...	...
3	...	...	...	...	...
4	...	...	...	...	...
5	...	...	...	...	...
6	...	...	...	...	...
7	...	...	...	...	...
8	...	...	...	...	...
9	...	...	...	...	...
10	...	...	...	...	...

...

from which the relative molal heat capacities listed in table 10 were calculated. The deviations given in table 10 are standard deviations.

Suppose we rearrange equation (18), substituting  $C_P^0(\text{He}) = 5/2 R$ . When we do this, we get the following expression:

$$\frac{C_P}{R} = 2.5 - \frac{1}{16(A_{0^{\circ}}/T_0)T^{5/4}} \left[ \left( 5b_1 + \frac{21b_2}{T^{1/2}} + \frac{45b_3}{T} \right) P + \left( 5c_1 + \frac{21c_2}{T^{1/2}} + \frac{45c_3}{T} \right) \frac{P^2}{2} \right] \quad (19)$$

from which the molal heat capacity values given in table 11 of this report were calculated. The deviations given in table 11 are standard deviations.

Joule-Thomson coefficients for helium at zero pressure for temperatures between  $0^{\circ}$  and  $150^{\circ}$  C were calculated as follows.  $\mu_{P=0}$  is defined by the equation

$$\mu_{P=0} = \left[ \left( \frac{dT}{dP} \right)_H \right]_{P=0} = - \frac{\left[ (\partial H / \partial P)_T \right]_{P=0}}{\left[ (\partial H / \partial T)_P \right]_{P=0}} \quad (20)$$

But  $\left[ (\partial H / \partial T)_P \right]_{P=0} = C_P^0$  and  $C_P^0$  for helium =  $2.5 R$ . Therefore,

$$\mu_{P=0} = - \frac{\left[ (\partial H / \partial P)_T \right]_{P=0}}{C_P^0} = - \frac{\left[ (\partial H / \partial P)_T \right]_{P=0}}{2.5 R} \quad (21)$$

We have previously shown that  $(\partial H / \partial P)_T$  is expressible by equation (12). Substituting equation (12) into equation (21),  $\mu_{P=0}$  is





TABLE 10. - Values of relative molal heat capacities,  $\frac{C_P - C_{P=0}}{R} = \frac{J}{R}$

<u>T, ° K</u>	<u>P, atm.</u> <u>0</u>	<u>P, atm.</u> <u>1</u>	<u>P, atm.</u> <u>5</u>	<u>P, atm.</u> <u>10</u>
273.15	0	-0.0001 ± 0.0000	-0.0006 ± 0.0002	-0.0012 ± 0.0003
275	0	-0.0001 ± 0.0000	-0.0006 ± 0.0002	-0.0012 ± 0.0003
300	0	-0.0001 ± 0.0000	-0.0005 ± 0.0001	-0.0010 ± 0.0002
325	0	-0.0001 ± 0.0000	-0.0004 ± 0.0001	-0.0008 ± 0.0002
350	0	-0.0001 ± 0.0000	-0.0003 ± 0.0001	-0.0007 ± 0.0001
375	0	-0.0001 ± 0.0000	-0.0003 ± 0.0000	-0.0006 ± 0.0001
400	0	-0.0001 ± 0.0000	-0.0003 ± 0.0000	-0.0005 ± 0.0001
425	0	-0.0000 ± 0.0000	-0.0002 ± 0.0000	-0.0005 ± 0.0000



TABLE 10. - Values of relative molal heat capacities,  $\frac{C_P - C_{P=0}}{R} = \frac{J}{R}$  (Con.)

<u>T, ° K</u>	<u>P, atm.</u> <u>20</u>	<u>P, atm.</u> <u>50</u>	<u>P, atm.</u> <u>75</u>	<u>P, atm.</u> <u>100</u>
273.15	-0.0023 ± 0.0007	-0.0052 ± 0.0015	-0.0071 ± 0.0021	-0.0086 ± 0.0026
275	-0.0023 ± 0.0007	-0.0052 ± 0.0015	-0.0070 ± 0.0021	-0.0085 ± 0.0026
300	-0.0019 ± 0.0005	-0.0043 ± 0.0011	-0.0059 ± 0.0015	-0.0072 ± 0.0019
325	-0.0016 ± 0.0003	-0.0036 ± 0.0008	-0.0050 ± 0.0011	-0.0062 ± 0.0014
350	-0.0013 ± 0.0003	-0.0031 ± 0.0006	-0.0044 ± 0.0008	-0.0055 ± 0.0010
375	-0.0012 ± 0.0002	-0.0027 ± 0.0004	-0.0039 ± 0.0006	-0.0049 ± 0.0007
400	-0.0010 ± 0.0001	-0.0024 ± 0.0003	-0.0035 ± 0.0004	-0.0045 ± 0.0005
425	-0.0009 ± 0.0001	-0.0022 ± 0.0002	-0.0032 ± 0.0003	-0.0041 ± 0.0004



TABLE 10. - Values of relative molal heat capacities,  $\frac{C_P - C_{P=0}}{R} = \frac{J}{R}$  (Con.)

<u>T, ° K</u>	<u>P, atm. 150</u>	<u>P, atm. 200</u>	<u>P, atm. 250</u>	<u>P, atm. 300</u>
273.15	-0.0101 ± 0.0033	-0.0096 ± 0.0037	-0.0073 ± 0.0039	-0.0031 ± 0.0041
275	-0.0100 ± 0.0033	-0.0096 ± 0.0036	-0.0074 ± 0.0038	-0.0033 ± 0.0040
300	-0.0087 ± 0.0024	-0.0089 ± 0.0026	-0.0078 ± 0.0027	-0.0053 ± 0.0029
325	-0.0078 ± 0.0017	-0.0084 ± 0.0019	-0.0080 ± 0.0020	-0.0066 ± 0.0021
350	-0.0071 ± 0.0013	-0.0080 ± 0.0014	-0.0081 ± 0.0015	-0.0075 ± 0.0016
375	-0.0066 ± 0.0009	-0.0076 ± 0.0010	-0.0081 ± 0.0011	-0.0081 ± 0.0011
400	-0.0061 ± 0.0007	-0.0073 ± 0.0007	-0.0081 ± 0.0008	-0.0085 ± 0.0008
425	-0.0057 ± 0.0005	-0.0070 ± 0.0005	-0.0080 ± 0.0005	-0.0087 ± 0.0006





TABLE 11. - Values of molal heat capacities,  $\frac{C_P}{R}$

<u>T, ° K</u>	<u>P,atm.</u> <u>0</u>	<u>P,atm.</u> <u>1</u>	<u>P,atm.</u> <u>5</u>	<u>P,atm.</u> <u>10</u>
273.15	2.5000	2.4999 ± 0.0000	2.4994 ± 0.0002	2.4988 ± 0.0003
275	2.5000	2.4999 ± 0.0000	2.4994 ± 0.0002	2.4988 ± 0.0003
300	2.5000	2.4999 ± 0.0000	2.4995 ± 0.0001	2.4990 ± 0.0002
325	2.5000	2.4999 ± 0.0000	2.4996 ± 0.0001	2.4992 ± 0.0002
350	2.5000	2.4999 ± 0.0000	2.4997 ± 0.0001	2.4993 ± 0.0001
375	2.5000	2.4999 ± 0.0000	2.4997 ± 0.0000	2.4994 ± 0.0001
400	2.5000	2.4999 ± 0.0000	2.4997 ± 0.0000	2.4995 ± 0.0001
425	2.5000	2.5000 ± 0.0000	2.4998 ± 0.0000	2.4995 ± 0.0000



TABLE 11. - Values of molal heat capacities,  $\frac{C_P}{R}$  (Con.)

<u>T, ° K</u>	<u>P, atm.</u> <u>20</u>	<u>P, atm.</u> <u>50</u>	<u>P, atm.</u> <u>75</u>	<u>P, atm.</u> <u>100</u>
273.15	2.4977 ± 0.0007	2.4948 ± 0.0015	2.4929 ± 0.0021	2.4914 ± 0.0026
275	2.4977 ± 0.0007	2.4948 ± 0.0015	2.4930 ± 0.0021	2.4915 ± 0.0026
300	2.4981 ± 0.0005	2.4957 ± 0.0011	2.4941 ± 0.0015	2.4928 ± 0.0019
325	2.4984 ± 0.0003	2.4964 ± 0.0008	2.4950 ± 0.0011	2.4938 ± 0.0014
350	2.4987 ± 0.0003	2.4969 ± 0.0006	2.4956 ± 0.0008	2.4945 ± 0.0010
375	2.4988 ± 0.0002	2.4973 ± 0.0004	2.4961 ± 0.0006	2.4951 ± 0.0007
400	2.4990 ± 0.0001	2.4976 ± 0.0003	2.4965 ± 0.0004	2.4955 ± 0.0005
425	2.4991 ± 0.0001	2.4978 ± 0.0002	2.4968 ± 0.0003	2.4959 ± 0.0004



TABLE 11. - Values of molal heat capacities,  $\frac{C_P}{R}$  (Con.)

<u>T, ° K</u>	<u>P, atm. 150</u>	<u>P, atm. 200</u>	<u>P, atm. 250</u>	<u>P, atm. 300</u>
273.15	2.4899 ± 0.0033	2.4904 ± 0.0037	2.4927 ± 0.0039	2.4969 ± 0.0041
275	2.4900 ± 0.0033	2.4904 ± 0.0036	2.4926 ± 0.0038	2.4967 ± 0.0040
300	2.4913 ± 0.0024	2.4911 ± 0.0026	2.4922 ± 0.0027	2.4947 ± 0.0029
325	2.4922 ± 0.0017	2.4916 ± 0.0019	2.4920 ± 0.0020	2.4934 ± 0.0021
350	2.4929 ± 0.0013	2.4920 ± 0.0014	2.4919 ± 0.0015	2.4925 ± 0.0016
375	2.4934 ± 0.0009	2.4924 ± 0.0010	2.4919 ± 0.0011	2.4919 ± 0.0011
400	2.4939 ± 0.0007	2.4927 ± 0.0007	2.4919 ± 0.0008	2.4915 ± 0.0008
425	2.4943 ± 0.0005	2.4930 ± 0.0005	2.4920 ± 0.0005	2.4913 ± 0.0006





expressible as

$$\mu_{P=0} = - \frac{1}{4T^{1/4} (2.5R)} \left( 5b_1 + \frac{7b_2}{T^{1/2}} + \frac{9b_3}{T} \right) \quad (22)$$

where  $R = (A_{0^\circ}/T_0)$ . We employed equation (22) in evaluating the  $\mu_{P=0}$  values for helium given in column 4 of table 12. The standard deviations of the  $\mu_{P=0}$  values calculated from equation (22) are also given in this table. These standard deviations were evaluated by expressing  $\mu_{P=0}$  in terms of the original data and applying the law for the "Propagation of Errors" (2, 5).



TABLE 12. - Joule-Thomson coefficients calculated from the original PVT data on helium obtained by Michels and Wouters

Curve	Zero Pressure-Temperature Intercept		$[(-\mu \times 10^2)_{P=0}]$	
	$^{\circ}$ C	$^{\circ}$ K	$^{\circ}$ K/atm.	
		273.150	0.000	$6.578 \pm 0.065$
		275.000	1.850	$6.569 \pm 0.063$
0		285.291	<u>1/</u> 12.141	$6.521 \pm 0.050$
		300.000	26.850	$6.460 \pm 0.035$
25		309.920	<u>1/</u> 36.770	$6.422 \pm 0.027$
		325.000	51.850	$6.369 \pm 0.018$
50		336.939	<u>1/</u> 63.789	$6.332 \pm 0.015$
		350.000	76.850	$6.294 \pm 0.016$
75		361.364	<u>1/</u> 88.214	$6.263 \pm 0.019$
		375.000	101.850	$6.229 \pm 0.023$
100		386.249	<u>1/</u> 113.099	$6.202 \pm 0.026$
		400.000	126.850	$6.172 \pm 0.030$
		425.000	151.850	$6.122 \pm 0.035$
150		438.564	<u>1/</u> 165.414	$6.097 \pm 0.037$

1/ Values reported in reference 1 for the average zero pressure-temperature intercept.



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## APPENDIX

The variances and covariances of the parameters appearing in equation (7) are

$$S_{b_1}^2 = 2.62073816 \times 10^{-8}$$

$$S_{b_2}^2 = 3.59370510 \times 10^{-5}$$

$$S_{b_3}^2 = 3.05540196 \times 10^{-3}$$

$$S_{c_1}^2 = 7.92910782 \times 10^{-13}$$

$$S_{c_2}^2 = 1.10592146 \times 10^{-9}$$

$$S_{c_3}^2 = 9.56817913 \times 10^{-8}$$

$$S_{b_1 b_2}^2 = -9.69954948 \times 10^{-7}$$

$$S_{b_1 b_3}^2 = 8.92894480 \times 10^{-6}$$

$$S_{b_1 c_1}^2 = -1.33199188 \times 10^{-10}$$

$$S_{b_1 c_2}^2 = 4.95015561 \times 10^{-9}$$

$$S_{b_1 c_3}^2 = -4.57577779 \times 10^{-8}$$

$$S_{b_2 b_3}^2 = -3.31177972 \times 10^{-4}$$

$$S_{b_2 c_1}^2 = 4.95085186 \times 10^{-9}$$

$$S_{b_2 c_2}^2 = -1.84191718 \times 10^{-7}$$



$$S_{b_2 c_3}^2 = 1.70451669 \times 10^{-6}$$

$$S_{b_3 c_1}^2 = -4.57756903 \times 10^{-8}$$

$$S_{b_3 c_2}^2 = 1.70495217 \times 10^{-6}$$

$$S_{b_3 c_3}^2 = -1.57961978 \times 10^{-5}$$

$$S_{c_1 c_2}^2 = -2.95963973 \times 10^{-11}$$

$$S_{c_1 c_3}^2 = 2.74817895 \times 10^{-10}$$

$$S_{c_2 c_3}^2 = -1.02806132 \times 10^{-8}$$

The above quantities were determined by expressing each constant in terms of the original observations and applying the law for the "Propagation of Errors." The standard deviation in any other calculated thermodynamic quantity evaluated from equation (8) can be determined from these variances and covariances.





