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# Heat Capacities of Gaseous Oxygen, Isobutane, and 1-Butene from $-30^{\circ}$ to $+90^{\circ}$ C

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An adiabatic constant-flow calorimeter previously used was modified to improve its accuracy. The heat capacity of gaseous oxygen was measured at  $-30^{\circ}$ ,  $+40^{\circ}$ , and  $+90^{\circ}$  C, and the results were compared with values calculated from spectroscopic data. The experimental and spectroscopic values agreed within 0.04, 0.02, and 0.11 percent at the three temperatures. The heat capacity of isobutane was measured at  $-30^{\circ}$ ,  $+0^{\circ}$ ,  $+40^{\circ}$ , and  $+80^{\circ}$  C. A few measurements were made on 1-butene at  $40^{\circ}$  and  $90^{\circ}$  C. Measurements on the hydrocarbons at two or more pressures permitted the calculation of values of  $(\partial^2 V/\partial T^2)_P$ .

## I. Introduction

In an earlier investigation [1]<sup>1</sup> an apparatus was described with which the specific heats of several hydrocarbons were measured with an accuracy of about one-half percent. Since this first paper, a study of the possible sources of error suggested some changes in the apparatus. These changes resulted in a significant improvement in accuracy. The apparatus was tested by making measurements on oxygen, whose specific heat is accurately known from spectroscopic data. The results of the test showed that errors in the present experimental results are probably less than one-tenth percent.

The testing of an apparatus for the determination of heat capacities of gases with a material whose heat capacity is well known is strongly recommended as the consistent error in this type of apparatus may be large compared with the random error.

The measurements of the heat capacities of isobutane and 1-butene provide data that are valuable in combination with spectroscopic data for the calculation of thermodynamic functions over a wide range of temperature. Such measurements are most useful when they cover a considerable temperature range with high accuracy.

## II. Materials

The impurities in the materials used in this investigation are believed to be of such nature and amounts as to have a negligible effect upon the specific heats.

The oxygen was prepared from water in a filter-press-type electrolytic generator used for the production of pure hydrogen in the Bureau's Cryogenic Laboratory. It was freed of hydrogen by passing the gas over hot palladium-coated asbestos. Then the oxygen was condensed and re-evaporated four times to remove water. The product is believed to be of especially high purity.

The isobutane, designated as Research Grade Lot No. 5, was obtained from the Phillips Petroleum Co. A determination of freezing-point lowering by the Thermochemistry and Hydrocarbons Section of the National Bureau of Standards showed that a sample from this lot contained  $0.12 \pm 0.06$  mole percent impurity. The sample in this investigation was found, by the Mass Spectrometry Section, to contain 0.04 mole percent diethyl ether and no more than 0.1 mole percent *n*-butane. No other impurity was found.

The 1-butene was supplied by the Phillips Petroleum Co. A measurement of freezing-point lowering made by J. G. Aston of Pennsylvania State College showed that a sample from the same batch had a liquid-soluble solid-insoluble impurity

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

of 0.46 percent. The Mass Spectrometry Section of the Bureau found the sample to contain 0.1 mole percent *n*-butane. They found no other impurity and were unable to detect any other butenes. However, the mass spectrometer would probably fail to detect less than 1 percent of other butenes.

### III. Apparatus and Procedure

The flow calorimeter is shown in vertical section in figure 1. This is the apparatus described by Scott and Mellors [1], except for the following changes suggested by some calculations of the heat transfer in the calorimeter by Harold W. Woolley: (1) The portion of the calorimeter tube between the cold compartment and the heater was lengthened from 41 to 56 mm in order to reduce heat conduction along the tube. The thimble, *Th*, was correspondingly lengthened from 21 to 36 mm. (2) To avoid thermal contact between the calorimeter tube and the shield, *S*, the cord between the bottom of the shield and the tube was removed. The shield was then centered and supported from the outside by means of cotton-cord spacers held in place by a brass washer.

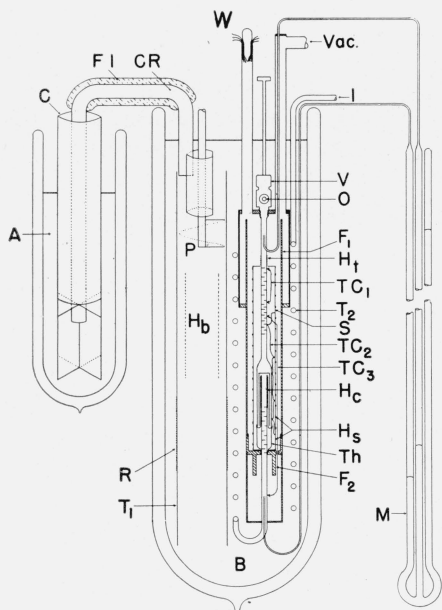


FIGURE 1.—Scale diagram of calorimeter

*A*, Liquid air; *C*, protecting cylinder; *FI*, felt insulation; *CR*, copper rod; *P*, propeller; *H<sub>b</sub>*, *H<sub>c</sub>*, *H<sub>s</sub>*, and *H<sub>a</sub>*, electric heaters; *R*, copper resistance thermometer; *T<sub>1</sub>*, stirrer tube; *W*, wax seal; *Vac.*, vacuum line; *I*, inlet; *V*, throttle valve; *O*, outlet; *F<sub>1</sub>*, flange; *TC<sub>1</sub>*, *TC<sub>2</sub>*, and *TC<sub>3</sub>*, thermocouples; *T<sub>2</sub>*, helical tube; *S*, radiation shield; *Th*, metal thimble; *F<sub>2</sub>*, flange; *B*, constant temperature bath; *M*, manometer.

The measurements of specific heats consisted of determinations of the rate of flow of the gas through the calorimeter, the electric power to the calorimeter heater, and the rise in temperature of the gas. Because of the pressure drop through the calorimeter and the resultant Joule-Thomson cooling, it was necessary to make auxiliary measurements of the decrease in the temperature of the gas flowing through the calorimeter when no power was supplied to the calorimeter heater.

The method of making the measurements was essentially the same as that previously described [1], although some improvements have been added. The following description is a brief review of the procedure, giving details only of the changes.

The gas entering the calorimeter was kept at nearly constant pressure by controlling the electric power supplied to an external boiler into which the material in the liquid state was introduced. The flow rate was fixed by setting the throttle valve, *V*, (fig. 1) at the beginning of an experiment. So that the flow rate might be as constant as possible, vapors on the low pressure side were condensed with liquid air. This was very satisfactory for condensing the hydrocarbons, but when oxygen was used the exhaust pressure was about 0.5 atmosphere. With oxygen, therefore, measurements of the specific heat at pressures below 1 atmosphere would not have been expected to be very accurate and were not carried out.

The rate of flow of the gas through the calorimeter was determined by condensing and weighing the gas that passed through in a measured time interval. Because the oxygen also was handled in this way, it was necessary to provide a weighing container of about 1 liter capacity that would safely hold a pressure of 100 atmospheres. Before starting to collect a sample to be weighed, a steady state was established with gas flowing to the waste container, and with the calorimeter heater turned on. Then the stream was diverted to the weighing container for a measured interval of time. In order to effect this change-over quickly and to measure the time interval accurately, the valve shown in section in figure 2 was designed. The gas from the calorimeter enters at *I* and can pass either to the waste container through *C<sub>1</sub>* or to the weighing container through *C<sub>2</sub>*, depending on the position of the double-ended valve needle, *N*. The needle is moved by the lever, *L*, which is operated through the strip of spring steel by the

handle, *H*. The metal bellows, *B*, provides a gas-tight seal, yet allows the lever to pivot about the pin, *P*. *Sw* is an electric switch that remains closed while the gas is flowing into the weighing container. This switch engages the clutch of a synchronous-interval timer. The motor of the interval timer is driven continuously by a standard 60-cycle signal furnished by the Central Radio Propagation Laboratory of the National Bureau of Standards. The time can be read to 0.01 second, and it is believed that the time of operating the

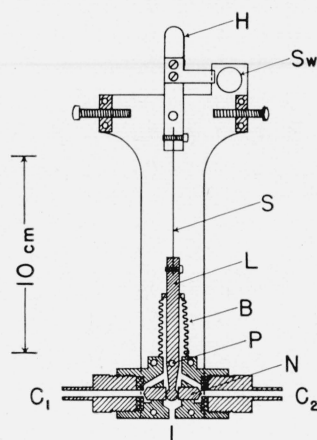


FIGURE 2.—Scale diagram of two-way valve.

*H*, Handle; *Sw*, electric switch; *L*, lever; *B*, metal bellows; *P*, pin; *N*, needle; *C*<sub>1</sub>, exit to waste container; *I*, gas inlet; *C*<sub>2</sub>, exit to weighing container; *S*, strip of spring steel.

valve is less than 0.1 second. The difference between the time taken to open and close the valve could not have caused a significant error in the heat capacity, as the minimum time for a determination was 600 seconds.

The data on 1-butene were taken before the installation of this valve and switch but, for these measurements, the runs were of sufficient duration so that errors in starting and stopping were not important. The principal advantage of this valve lies in the fact that the flow, and therefore the equilibrium temperatures, are relatively undisturbed when the flow is diverted from one collecting reservoir to the other.

The power input to the calorimeter was determined with a Wenner potentiometer by measuring the current flowing through the heater and the potential drop across it. The temperature rise of the gas was measured by means of a five-junction copper-constantan difference thermocouple, *TC*<sub>3</sub>. The wires of this couple make

three turns around both the radiation shield and the flange, *F*<sub>2</sub>, and are cemented with Glyptal lacquer. This brought the leads to the approximate temperatures of the junctions and so prevented significant differences between the temperatures of the thermocouple junctions and the adjacent parts of the calorimeter tube. The fact that the thermocouple was not calibrated in place is not believed to have caused an appreciable error as no significant differences in potential were found when the thermocouple was immersed varying amounts in the calibration bath, and as strains were avoided in those parts of the thermocouple in which there were temperature gradients. Further, the calibration of the thermocouple is not believed to have changed with time, as no significant differences in potential were observed between points taken 2 months apart in the calibration of the thermocouple used in the present investigation. It is believed that the temperature intervals in the heat capacity measurements were determined to about one part in 5,000.

Small variations in the temperature rise of the gas,  $\Delta t$ , perhaps caused by small changes in the power input to the calorimeter heater, *H*<sub>c</sub>, were compensated for by small adjustments of the input pressure. In this way, the temperature rise of about 10 degrees was maintained constant to about 0.01 degree. Furthermore, when a run was terminated,  $\Delta t$  was very constant and had the same value (within 0.001°) that it had at the start of the run. Thus the heat capacity of the calorimeter did not enter into the computations.

The Joule-Thomson correction for all three gases was determined by measuring the temperature decrease when gas was passed through the calorimeter without applying heat to the calorimeter tube, but with all other conditions the same as in a specific-heat run. These measurements were made at temperatures equal to the mean temperatures of the specific-heat runs and at various pressure drops and mean pressures. These measurements may include effects other than the Joule-Thomson effect and are more accurately called blank runs. The probable error in the heat capacity caused by the uncertainty in the blank runs is estimated as 0.03 percent.

#### IV. Test of the Apparatus with Oxygen

The heat capacity of oxygen was measured to test the accuracy obtainable with the calorimeter

after making the changes described in section III. Oxygen was used for this purpose because the specific heat is accurately known from spectroscopic data, and it could be condensed and weighed.

### 1. Observed Data

The observed heat capacity,  $C_P$ , in calories per mole-degree, was calculated from the relation

$$C_P = \frac{WM}{4.1833r(\Delta t + \delta t)}, \quad (1)$$

where  $W$  is the heat input in watts,  $r$  is the flow rate in grams per second,  $M$  is the molecular weight,  $\Delta t$  is the temperature rise, and  $\delta t$  is the Joule-Thomson cooling in degrees centigrade.

Equation 1 actually gives values of  $\Delta H/\Delta T$ , but for the temperature intervals chosen for these experiments  $\Delta H/\Delta T = dH/dT = C_P$  within the precision of the data.

The determinations of the heat capacity of oxygen consist of three groups of measurements with mean temperatures of approximately  $-30^\circ$ ,  $+40^\circ$ , and  $+90^\circ$  C.

The data of each group were adjusted to a common temperature by using the observed temperature dependence of the heat capacity. The adjustments were so small that they introduced no appreciable error. The original data and the heat capacities, before and after adjustment for temperature, are given in table 1, and in figure 3 the adjusted data are plotted.

TABLE 1.—Heat capacities of oxygen<sup>1</sup>

Mass of material	Mean temperature	Mean pressure	Temperature rise	Pressure drop in calorimeter	Joule-Thomson temperature fall	Flow rate	Power	$\frac{\Delta T}{W}$	$C_P$	$C_P$ adjusted to temperature, $t$
<i>g</i>	$^\circ$ C	<i>mm</i> Hg	$^\circ$ C	<i>mm</i> Hg	$^\circ$ C	<i>g sec</i> <sup>-1</sup>	<i>Watt</i>	$^\circ$ C <i>watt</i> <sup>-1</sup>	<i>cal mole</i> <sup>-1</sup> $^\circ$ C <sup>-1</sup>	<i>cal mole</i> <sup>-1</sup> $^\circ$ C <sup>-1</sup> <i>t</i> = $-30^\circ$ C
31.680	-29.75	764	10.468	20	0.007	0.021999	0.21085	49.7	6.999	6.998
38.595	-29.83	768	10.297	20	.007	.022181	.20883	49.3	6.989	6.989
16.390	-29.91	775	10.131	21	.007	.022764	.21107	48.0	6.996	6.996
32.047	-29.68	791	10.602	134	.047	.059226	.57666	18.5	6.994	6.993
32.583	-29.78	783	10.390	140	.048	.060331	.57563	18.1	6.992	6.992
43.540	-29.28	799	11.389	139	.048	.060472	.63222	18.1	6.992	6.991
60.774	-30.01	798	9.880	263	.089	.084394	.76852	13.0	6.988	6.988
50.680	-30.03	798	9.849	265	.089	.084462	.76808	12.9	7.000	7.000
60.841	-29.99	790	9.920	267	.090	.084503	.77303	12.9	6.991	6.991
25.885	39.61	757	9.124	8	.002	.011524	.09719	93.9	7.069	7.069
22.040	39.69	750	9.291	21	.006	.019357	.16595	56.0	7.054	7.054
24.763	39.62	751	9.158	21	.006	.019649	.16585	55.3	7.046	7.047
46.538	39.90	737	9.794	78	.024	.038328	.34659	28.3	7.045	7.045
56.005	39.89	763	9.682	141	.043	.052962	.47506	20.5	7.055	7.055
41.337	40.21	796	10.338	138	.041	.053000	.50688	20.5	7.049	7.049
70.156	40.21	796	10.311	138	.041	.053096	.50637	20.4	7.048	7.047
65.746	40.39	812	10.772	179	.055	.061240	.61030	17.7	7.041	7.040
67.440	39.93	780	9.860	217	.066	.066652	.60926	16.3	7.044	7.044
46.571	40.02	765	9.952	249	.072	.070601	.65213	15.4	7.049	7.049
47.046	41.54	773	13.001	251	.072	.071256	.85924	15.2	7.056	7.054
64.210	39.96	768	9.841	253	.073	.071351	.65223	15.2	7.053	7.053
51.428	39.95	767	9.823	254	.074	.071467	.65182	15.2	7.049	7.049
25.275	89.30	738	8.690	12	.004	.013242	.10713	81.2	7.118	7.119
34.818	89.80	720	9.686	22	.007	.018055	.16281	59.5	7.116	7.116
26.573	89.73	732	9.542	51	.015	.028250	.25131	38.0	7.120	7.121
36.511	89.58	765	9.162	48	.016	.028299	.24165	38.0	7.117	7.118
55.485	89.68	760	9.462	92	.027	.039132	.34578	27.4	7.123	7.124
45.422	89.86	771	9.794	91	.027	.039432	.36091	27.2	7.129	7.129

<sup>1</sup> One calorie is defined as 4.1833 int. j.

## 2. Heat Leak

The heat leak of the calorimeter was determined by measuring heat capacities at varying flow rates, but the leak was found to be so small that no correction was made. The smallness of the leak is confirmed by heat transfer calculations

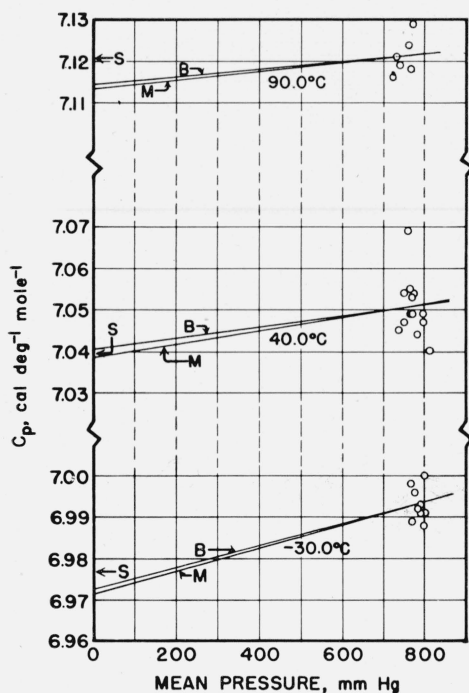


FIGURE 3.—Experimental results for oxygen.

B, Beattie-Bridgeman equation; M, Meyers equation; S, Spectroscopic value.

and especially by the agreement between the spectroscopic and experimental values for oxygen.

### 3. Comparison of the Experimental and Spectroscopic Heat Capacities

In order to compare the observed heat capacities with those calculated from spectroscopic data, it is necessary to obtain  $C_P - C_P^\circ$ . This was calculated by means of the general thermodynamic relationship

$$C_P - C_P^\circ = \int_0^P T(\partial^2 V / \partial T^2)_P dP, \quad (2)$$

and with the aid of the Beattie-Bridgman equation

[2] and an equation<sup>2</sup> developed by Meyers [3] especially for oxygen.

The effect of the reduction to the ideal gas state may be seen both in table 2 and figure 3, in which the experimental averages of  $C_{P, \text{real}}$  are reduced to the ideal gas state and compared with the spectroscopic values. In table 2, groups of heat-capacity data are adjusted to a common pressure as well as temperature in order to facilitate comparison of the data. It may be seen that the experimental and spectroscopic values of the heat capacity agree within 0.04, 0.02, and 0.11 percent at  $-30^\circ$ ,  $+40^\circ$ , and  $+90^\circ$  C, respectively.

TABLE 2.—Comparison of measured and spectroscopic values of the heat capacity of oxygen<sup>1</sup>

Temperature ° C	Mean $C_P$ for 1 atm <i>cal mole<sup>-1</sup> ° C<sup>-1</sup></i>	$C_P^\circ$ calculated from column 2 by using $C_P - C_P^\circ$ from—		$C_P^\circ$ derived from spectro- scopic data <sup>2</sup> <i>cal mole<sup>-1</sup> ° C<sup>-1</sup></i>
		Meyers equation <i>cal mole<sup>-1</sup> ° C<sup>-1</sup></i>	Beattie- Bridgeman equation <i>cal mole<sup>-1</sup> ° C<sup>-1</sup></i>	
-30	6.993	6.972	6.973	6.976 <sub>5</sub>
40.04	7.050	7.038	7.040	7.039 <sub>6</sub>
90	7.121	7.113	7.114	7.120 <sub>9</sub>

<sup>1</sup> One calorie is defined as 4.1833 int. j.

<sup>2</sup> These values are obtained by interpolation in an unpublished table prepared by H. W. Woolley of the National Bureau of Standards, in which he has adjusted Johnston and Walker's [19] values for more recent values of the vibrational frequency [20], the radiation constant  $c_2$  (1.4284 cm ° C<sup>-1</sup>) and the gas constant (1.98714 cal mole<sup>-1</sup> ° C<sup>-1</sup>).

## V. Results of Measurements on Isobutane and 1-Butene

### 1. Observed Data

The data for isobutane and 1-butene are presented in table 3 and in figures 4 and 5. Observations were made at two or more pressures, except for the data on 1-butene at  $90^\circ$  C. At  $-30^\circ$  C the measurements on isobutane were made at rather low pressures to avoid condensation of the gas as it passed through the calorimeter. The computations follow the plan used for oxygen (section IV).

<sup>2</sup>  $PV/RT = 1 + BV^{-1} + CV^{-2} + EV^{-4}$ , where the coefficients B, C, and E have the values  $B, -0.006772T_c(1 - 10^{-0.54257T_c/T}) + 0.0009878$ ;  $C, 4.2 \times 10^{-6} T_c(1 - 10^{-0.84823(T_c/T^3)}) + 1.426 \times 10^{-6}$ ;  $E, -7.35 \times 10^{-12} T_c(1 - 10^{-2.0709(T_c/T^7)}) + 5.55 \times 10^{-12}$ .

TABLE 3.—Heat capacities of isobutane and 1-butene <sup>a</sup>

Mass of material	Mean temperature	Mean pressure	Temperature rise	Pressure drop in calorimeter	Joule-Thomson temperature fall	Flow rate	Power	$\frac{\Delta T}{W}$	$C_P$	$C_P$ adjusted to temperature, $t$
ISOBUTANE										
$g$	$^{\circ}C$	$mm\ Hg$	$^{\circ}C$	$mm\ Hg$	$^{\circ}C$	$g\ sec^{-1}$	$Watt$	$^{\circ}C\ watt^{-1}$	$cal\ mole^{-1}\ ^{\circ}C^{-1}$	$cal\ mole^{-1}\ ^{\circ}C^{-1}$
24.380	-29.96	90	10.146	74	0.186	0.020309	0.29860	34.6	19.770	19.767
27.160	-29.97	94	9.980	78	.194	.020618	.29862	34.1	19.779	19.777
18.421	-30.05	91	9.949	76	.190	.020798	.30021	33.8	19.780	19.783
14.258	-29.95	180	10.047	18	.051	.013766	.19912	50.7	19.901	19.898
17.384	-29.99	178	9.978	18	.051	.013800	.19828	50.6	19.905	19.905
19.070	-30.00	179	9.964	18	.051	.013832	.19838	50.5	19.897	19.897
14.599	-30.06	180	9.824	48	.126	.022123	.31468	31.6	19.862	19.866
23.985	-30.03	176	9.868	47	.125	.022208	.31749	31.5	19.876	19.877
20.839	-29.96	178	10.042	84	.207	.030139	.44247	23.2	19.901	19.898
31.172	-29.99	180	9.973	85	.209	.030498	.44451	22.9	19.888	19.888
30.058	-30.07	176	9.826	96	.230	.030754	.44204	22.7	19.858	19.862
19.094	-29.99	233	9.938	36	.098	.022179	.31949	31.4	19.941	19.941
16.014	-29.91	228	10.071	36	.098	.022266	.32532	31.3	19.962	19.954
19.723	-29.91	227	10.080	36	.098	.022283	.32543	31.3	19.935	19.927
										$t=0^{\circ}C$
13.664	.11	189	10.211	29	.055	.016868	.26982	38.0	21.649	21.642
13.194	.09	189	10.178	29	.055	.016917	.26992	37.9	21.662	21.657
15.337	-.06	378	9.870	6	.013	.011343	.17600	56.2	21.812	21.817
12.267	-.02	390	9.968	6	.013	.011498	.18019	55.4	21.814	21.815
14.252	-.06	378	9.859	14	.028	.016964	.26312	37.6	21.796	21.800
14.754	-.13	390	9.748	29	.055	.024585	.37803	25.9	21.790	21.799
23.247	.06	380	10.093	40	.075	.028407	.45294	22.4	21.786	21.782
19.116	-.08	390	9.847	39	.073	.028605	.44517	22.3	21.796	21.801
										$t=40^{\circ}C$
12.979	39.78	184	9.568	36	.044	.017248	.28816	33.4	24.148	24.162
10.882	39.83	189	9.667	36	.044	.017250	.29124	33.3	24.155	24.166
13.213	40.23	389	10.451	8	.010	.011584	.21151	49.5	24.249	24.235
15.992	40.22	390	10.445	8	.010	.011587	.21151	49.4	24.258	24.244
18.051	40.04	387	10.082	15	.019	.016276	.28692	35.2	24.247	24.244
16.144	40.04	390	10.081	15	.019	.016290	.28701	34.8	24.235	24.233
41.364	40.33	387	10.662	61	.072	.032812	.61531	17.4	24.272	24.251
42.594	40.01	390	10.026	61	.072	.033065	.58258	17.3	24.241	24.241
										$t=80^{\circ}C$
14.886	79.72	185	9.439	22	.021	.012845	.23368	40.5	26.718	26.736
10.715	79.65	190	9.305	23	.021	.013201	.23696	39.4	26.740	26.763
14.054	79.64	391	9.272	22	.021	.018804	.33661	27.6	26.763	26.785
19.178	79.65	391	9.299	22	.021	.018811	.33784	27.6	26.772	26.795
28.436	80.30	387	10.604	56	.046	.029578	.60819	17.5	26.824	26.804
20.911	79.73	392	9.463	57	.047	.030230	.55438	17.2	26.792	26.809
18.226	79.72	391	9.431	58	.048	.030351	.55447	17.1	26.777	26.795
1-BUTENE										
										$t=40.4^{\circ}C$
10.632	40.43	372	10.874	6	0.008	0.009763	0.17126	63.5	21.619	21.615
24.495	40.52	371	11.050	14	.020	.015402	.27438	40.3	21.583	21.576
36.162	40.41	367	10.845	39	.054	.025733	.45110	24.2	21.571	21.571
62.818	40.34	369	10.703	99	.131	.041426	.72207	15.0	21.578	21.580
30.343	40.34	749	10.905	12	.016	.020285	.35944	30.4	21.760	21.763
41.559	40.35	747	10.920	23	.031	.028309	.50298	21.8	21.760	21.763
72.130	40.46	748	11.149	46	.062	.040318	.73372	15.3	21.771	21.768
67.243	40.44	749	11.091	98	.128	.059892	1.09059	10.3	21.768	21.765
										$t=90.1^{\circ}C$
16.148	89.97	754	9.867	4	.004	.010892	.19503	50.6	24.328	24.335
25.067	90.14	749	10.200	12	.010	.018669	.34582	29.5	24.332	24.330
55.472	90.18	748	10.288	50	.044	.039031	.73217	14.1	24.350	24.346
100.234	90.04	748	9.991	102	.089	.056021	1.02485	9.8	24.340	24.343

<sup>a</sup> One calorie is defined as 4.1833 int. j. The molecular weight of isobutane was taken as 58.120, and that of 1-butene as 56.104.

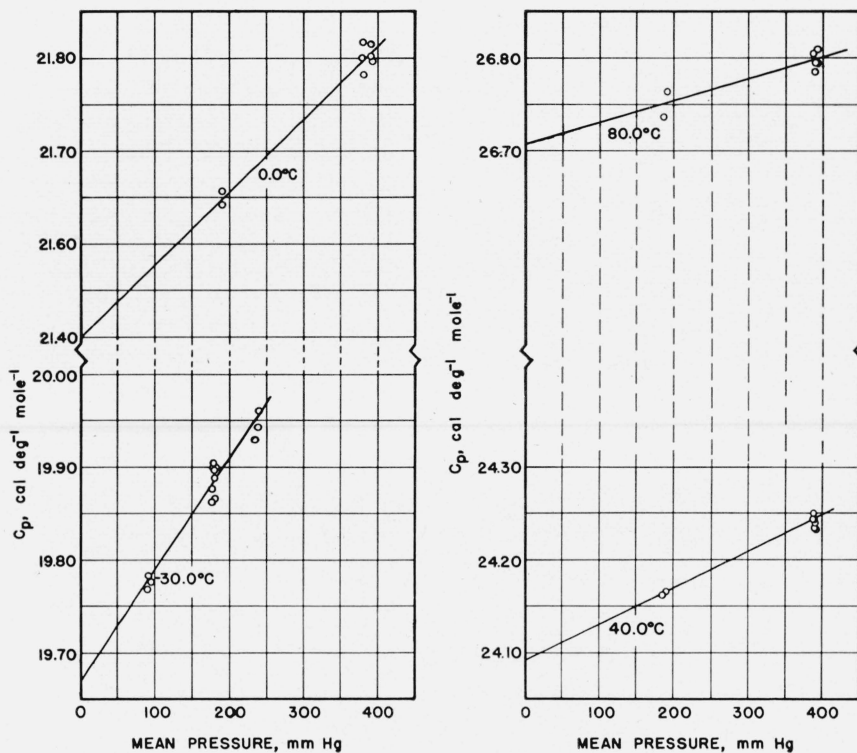


FIGURE 4.—Experimental results for isobutane.

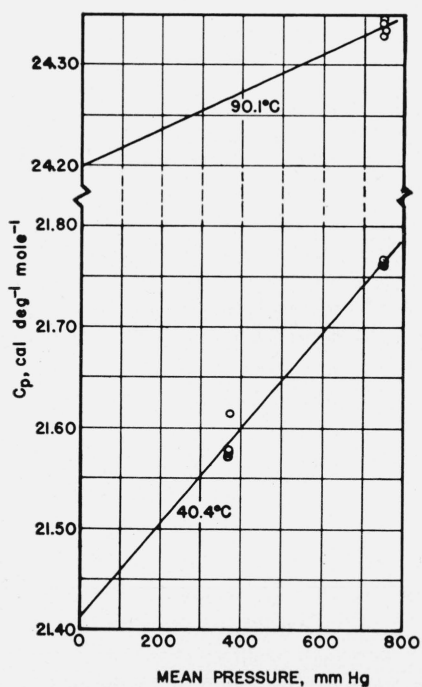


FIGURE 5.—Experimental results for 1-butene.

## 2. Reduction of the Specific Heat to the Ideal Gas State

### (a) Isobutane

In order to obtain  $C_P^\circ$ , the heat capacity data for a given temperature were plotted against pressure and extrapolated linearly to zero pressure (fig. 4). The results are given in column 6 of table 4.

Waddington, Todd, and Huffman [4], who determined the heat capacity of *n*-heptane and 2,2,3-trimethylbutane, also extrapolated their data linearly to obtain  $C_P^\circ$  values.

Values of  $C_P - C_P^\circ$  obtained by extrapolation are considered the most reliable; however, for the purposes of comparison, column 4 of table 4 gives the values of  $C_P^\circ$  obtained by using published critical constants [5] in the Berthelot equation, and column 5 gives the values of  $C_P^\circ$  obtained by using the constants of Benedict, Solomon, and Rubin [6] in their Kellogg equation. The experimental data used to determine the constants of the Kellogg equation consisted of measurements

of the liquid-vapor equilibrium in the methane-ethylene-isobutane system.

TABLE 4.—Heat capacities of isobutane in the real and ideal states<sup>1</sup>

Temperature	Pressure	Mean <sup>2</sup> $C_{P, \text{real}}$	$C_P^\circ$ calculated from column 3 by using $C_P - C_P^\circ$ from—			$(\partial^2 V / \partial T^2)_P$ from heat capacity measurements
			Berthelot equation <sup>2</sup>	Kellogg equation <sup>3</sup>	Heat-capacity measurements	
$^\circ\text{C}$	mm Hg	$\frac{\text{cal}}{\text{mole}} \text{ } ^\circ\text{C}^{-1}$	$\frac{\text{cal}}{\text{mole}} \text{ } ^\circ\text{C}^{-1}$	$\frac{\text{cal}}{\text{mole}} \text{ } ^\circ\text{C}^{-1}$	$\frac{\text{cal}}{\text{mole}} \text{ } ^\circ\text{C}^{-1}$	$\frac{\text{liter mole}}{^\circ\text{C}^2}$
-30	92	19.777	19.699	19.657	19.669	$15_2 \times 10^{-6}$
-30	178	19.886	19.735	19.653		
-30	229	19.940	19.745	19.641	21.503	8 <sub>9</sub>
0	189	21.650	21.537	21.490		
0	384	21.802	21.572	21.476	24.095	3 <sub>5</sub>
40	186	24.165	24.091	24.071		
40	389	24.242	24.087	24.046	26.705	2 <sub>1</sub>
80	188	26.750	26.698	26.689		
80	390	26.797	26.689	26.671		

<sup>1</sup> One calorie is defined as 4.1833 int. j, and the molecular weight of isobutane is taken as 58.120.

<sup>2</sup> The values of  $C_P$  were adjusted to the indicated temperatures and then averaged to facilitate correlation.

<sup>3</sup> These values were computed for comparison only. The values in column 6 are considered most reliable.

Values of  $(\partial^2 V / \partial T^2)_P$  were calculated from the change with pressure of the calorimetrically determined heat capacities by means of eq 2, assuming that  $C_P - C_P^\circ$  is proportional to pressure. The results are presented in column 7 of table 4.

### (b) 1-Butene

For 1-butene at 40.4° C, the correction to the ideal gas state was assumed to be proportional to the pressure and  $C_P^\circ$  was obtained from calorimetric data by extrapolation to zero pressure (column 7 of table 5) as was done for isobutane. This procedure was chosen because the published data of state for 1-butene are more inadequate than for isobutane. To show the inadequacy of the equations of state for calculating reliable values of  $C_P - C_P^\circ$ , columns 4, 5, and 6 were included in table 5 giving the values of  $C_P^\circ$  obtained with the Berthelot equation [7, 8], Meyers equation for the density of saturated vapors [9, 10, 11], and a previously used [12, 13] empirical equation.

$$PV/RT = 1 - k/VT^2 \quad (3)$$

The value of  $k$  was estimated as  $1.01 \times 10^{-6}$  ml deg<sup>2</sup> g<sup>-1</sup> from the vapor density data of Roper [14]

and of Aston, Fink, Bestul, Pace, and Szasz [15]. It may be seen that the values of  $C_P^\circ$ , calculated with the equations of state, vary more with pressure than is consistent with the accuracy of the calorimetric data. The recently published  $P$ - $V$ - $T$  data of Olds, Sage, and Lacey [16] are not sufficiently precise to give good values of  $(\partial^2 V / \partial T^2)_P$ .

TABLE 5. Heat capacities of 1-butene in the real and ideal states<sup>1</sup>

Temperature	Pressure	Mean <sup>2</sup> $C_{P, \text{real}}$	$C_P^\circ$ calculated from column 3, using $C_P - C_P^\circ$ from—				$(\partial^2 V / \partial T^2)_P$ from heat capacity measurements
			Berthelot equation <sup>4</sup>	Meyers equation <sup>4</sup>	Equation 3 <sup>4</sup>	Heat capacity measurements	
$^\circ\text{C}$	mm Hg	$\frac{\text{cal}}{\text{mole}} \text{ } ^\circ\text{C}^{-1}$	$\frac{\text{cal}}{\text{mole}} \text{ } ^\circ\text{C}^{-1}$	$\frac{\text{cal}}{\text{mole}} \text{ } ^\circ\text{C}^{-1}$	$\frac{\text{cal}}{\text{mole}} \text{ } ^\circ\text{C}^{-1}$	$\frac{\text{cal}}{\text{mole}} \text{ } ^\circ\text{C}^{-1}$	$\frac{\text{liter mole}}{^\circ\text{C}^2}$
40.4	370	21.586	21.439	21.458	21.452	21.411	$4_6 \times 10^{-6}$
40.4	748	21.765	21.468	21.498	21.487		
90.1	750	24.338 <sup>2</sup>	24.146	-----	24.162	<sup>2</sup> 24.19	

<sup>1</sup> One calorie is defined as 4.1833 int. j and the molecular weight of 1-butene is taken as 56.104.

<sup>2</sup> This value was calculated as described in section V-2-b.

<sup>3</sup> The values of  $C_P$  were adjusted to the indicated temperatures and then averaged to facilitate correlation.

<sup>4</sup> These values were computed for comparison only. They indicate that the equations of state are not adequate for determining the correction to the ideal gas state.

At 90.1° measurements of  $C_P$  were made only at 750 mm Hg, and so the correction cannot be determined by extrapolation of the calorimetric data to zero pressure. The correction for 1-butene at 90.1° was computed from that at 40.4°, assuming that the ratio of the two corrections was the same as that found experimentally for isobutane.

## VI. Estimate of Accuracy

As shown in section IV-3, the experimental values of the heat capacity of oxygen agree with those calculated from spectroscopic data within 0.04, 0.02, and 0.11 percent at -30°, +40°, and +90°C, respectively. If there is no significant difference between the relative accuracies of the data for oxygen and the hydrocarbons, and there is no evidence for such a difference, then the probable error of the mean values of  $C_{P, \text{real}}$  presented in this paper should be roughly 0.07 percent. This value is in agreement with the probable error of 0.06 percent estimated from a consideration of the known sources of error.



## VII. Comparison With the Work of Other Observers

A search of the literature failed to show either experimental heat-capacity data for oxygen with an accuracy comparable with that of the present measurements or reliable experimental heat-capacity data for 1-butene.

The heat capacity of isobutane has been measured by Dailey and Felsing [17] and by Sage, Webster, and Lacy [18]. The results of Dailey and Felsing agree with those obtained in this investigation within their estimated error (up to 1 percent) in the temperature range covered by both investigations. The values of Sage, Webster, and Lacey fall considerably below the results of this investigation and that of Dailey and Felsing. The data of the former were reduced to the ideal gas state with the Berthelot equation, but any error in the equation would be small in comparison with

the differences between their data and those reported here. All the data for isobutane are presented in figure 6.

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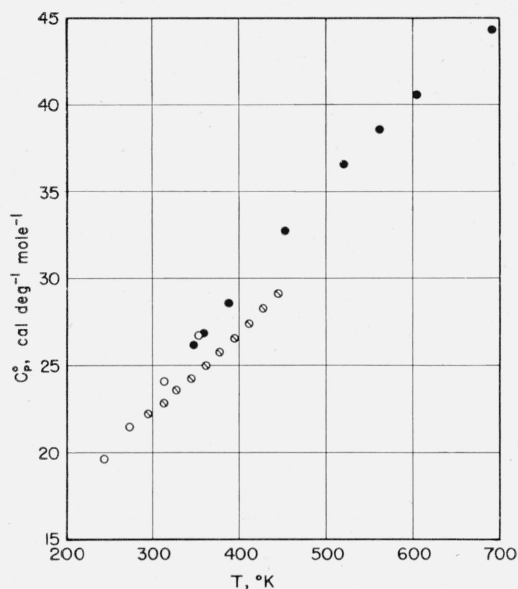


FIGURE 6.—Comparison of results for isobutane with those of other investigators.

●, Dailey and Felsing; ○, Sage, Webster, and Lacey; ○, this investigation.