SPECIFIC HEATS OF GASEOUS 1,3-BUTADIENE, ISOBUTENE, STYRENE, AND ETHYLBENZENE

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ABSTRACT

This paper describes a flow calorimeter and measurements of the specific heats
of four hydrocarbons that are of interest in connection with synthetic rubber.
The measurements on gaseous 1,3-butadiene and isobutene cover the range
−35° to +80° C. The specific heats of styrene vapor and ethylbenzene vapor
were determined at 100° C. The calorimeter was tested by measuring the specific
heat of normal hydrogen. The results on the hydrocarbons are believed to be
correct to ±0.5 percent.

CONTENTS

I. INTRODUCTION

The measurements described in this paper were undertaken at
the Bureau as part of a program of obtaining thermal data on the
properties of materials of interest in connection with synthetic rubber.
The compounds studied in the present investigation are among the
most important of the materials used in the synthetic-rubber industry.
Butadiene and styrene are the principal ingredients of GR–S (Govern-
ment rubber-styrene type). Isobutene is copolymerized with iso-
prene in the manufacture of butyl rubber. Ethylbenzene is converted
into styrene by dehydrogenation, this process supplying most of
the styrene used.

The calorimeter used was of the adiabatic constant-flow type, designed to have a small resistance to flow so that measurements could be made on vapors of low saturation pressure. The specific heats of gaseous butadiene and isobutene were measured at four temperatures between −35° and 80° C. Because of the low vapor pressures of styrene and ethylbenzene, the specific heats of their vapors were measured at only one temperature, 100° C. The apparatus was tested by measuring the specific heat of normal hydrogen.

The specific-heat data obtained are useful for comparison with calculations of thermodynamic properties based on spectroscopic data, calculations which were made to extend to higher temperature tables of calorimetric properties determined at low temperatures.

II. MATERIALS

The samples of hydrocarbons used in this investigation were obtained from several different sources. The impurities in the various samples are believed to be so small as to have a negligible effect on the specific heat results. The sources and estimated purities of the samples are given below.

1. BUTADIENE

The 1,3-butadiene was furnished by the Dow Chemical Co. It was stated to contain about 0.2 mole percent of impurity. A small amount of polymer in the liquid would not affect the results because the vapor was supplied to the calorimeter from a boiler, and the polymer of low vapor pressure would remain in the boiler. This applies also to isobutene and styrene.

2. ISOBUTENE

The isobutene was furnished by the Standard Oil Development Co. The purity of the sample used was not directly determined, but measurements on other samples from the same cylinder indicate that its purity was higher than 99 mole percent.

3. STYRENE

The styrene was supplied by the Dow Chemical Co. The liquid soluble, solid insoluble, impurity calculated from the freezing point was 0.75 mole percent. Tertiary-butyl-catechol (0.005 percent by weight) was added to the liquid to reduce the rate of polymerization.

4. ETHYLBENZENE

The ethylbenzene was part of a sample distilled by M. R. Fenske, of the Petroleum Refining Laboratory of The Pennsylvania State College. The physical constants reported by The Pennsylvania State College were: 50 percent, Cottrell boiling point 136.25° C; index of refraction $n_D^{20}=1.4958$. The freezing point, measured by Alfred Matuszak at American Petroleum Institute Laboratories of Ohio State University was −95.02° C. The amount of impurity in this sample appears to be of the order of 0.2 mole percent.

III. APPARATUS

The calorimeter used for this investigation was of the constant flow, adiabatic type. Some important features of design were adapted from the flow calorimeter of Osborne, Stimson, and Sligh [1].[1] Simplifications were introduced to make the construction less difficult. The resistance to flow was reduced so that gases of low saturation pressure could be passed through the calorimeter at satisfactory rates. The maximum pressure drop through the calorimeter during the present experiments was 46 millimeters of mercury, observed when passing butadiene through the calorimeter at a mean pressure of 90 millimeters of mercury, at a rate of 1 gram per minute. The heat capacity of the internal part of the calorimeter was kept small to facilitate the establishment of thermal equilibrium with a small flow of gas. As it was desired also to measure the specific heat of vapors (other than hydrocarbons) that corrode copper and silver, the use of these metals was avoided in the construction of certain parts of the calorimeter. This was a disadvantage, since the high thermal conductivity of copper or silver is desirable where isothermal surfaces are wanted. All parts of the apparatus traversed by the gas are made of monel tubing of 0.010-inch wall thickness.

Figure 1 is a scale diagram of the principal parts of the apparatus. The calorimeter is immersed in the bath, B, the temperature of which is controlled by supplying electric power to the heater, H_b. The propeller, P, forces the liquid down through the tube, T_1. On the outside of this tube near the bottom is the resistor, R, consisting of about 140 ohms of No. 37 AWG copper wire, which forms one arm of a Wheatstone bridge circuit. The galvanometer in this circuit will respond to a change in temperature of the bath of less than 0.001° C, and it is not difficult, by manual control, to keep the bath temperature constant to 0.002 or 0.003 degree centigrade. The arrangement shown at the left side of the diagram is used to cool the bath when operating below room temperature. It consists of a copper rod, CR, which conducts heat from the bath into the liquid air, A. Vanes of sheet copper are soldered to each end of the rod to improve thermal contact with the liquids. The brass tube, C, closed at the bottom prevents the liquid air from coming into contact with the copper rod, except at the lower end. This makes the rate of heat transfer almost independent of the depth of the liquid air.

The gas being investigated enters at I and passes through the helical tube, T_2, where it is brought to the temperature of the bath. The tube, T_2, enters the evacuated chamber at the bottom. The gas passes through a system of baffles in the tube and then is heated by the calorimeter heater, H_c, which consists of about 14 ohms of No. 34 AWG constantan wire with fiber-glass insulation. At this point the direction of flow of the gas is reversed so that it passes down through the annular space surrounding the heater. The heater is not in the gas stream but lies between the two inner coaxial tubes. The gas then enters the outside annular space and flows upward again and enters the small part of the tube where it passes through another system of baffles. By the time the gas reaches this region any non-uniformity in temperature, which may have existed near the heater,

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[1] Figures in brackets indicate the literature reference at the end of this paper.

should have disappeared. The baffles in the tube are intended to obstruct radiation along the tube and to promote thermal equilibrium between the gas stream and the wall of the tube. The gas leaves the calorimeter through the throttle valve, V.
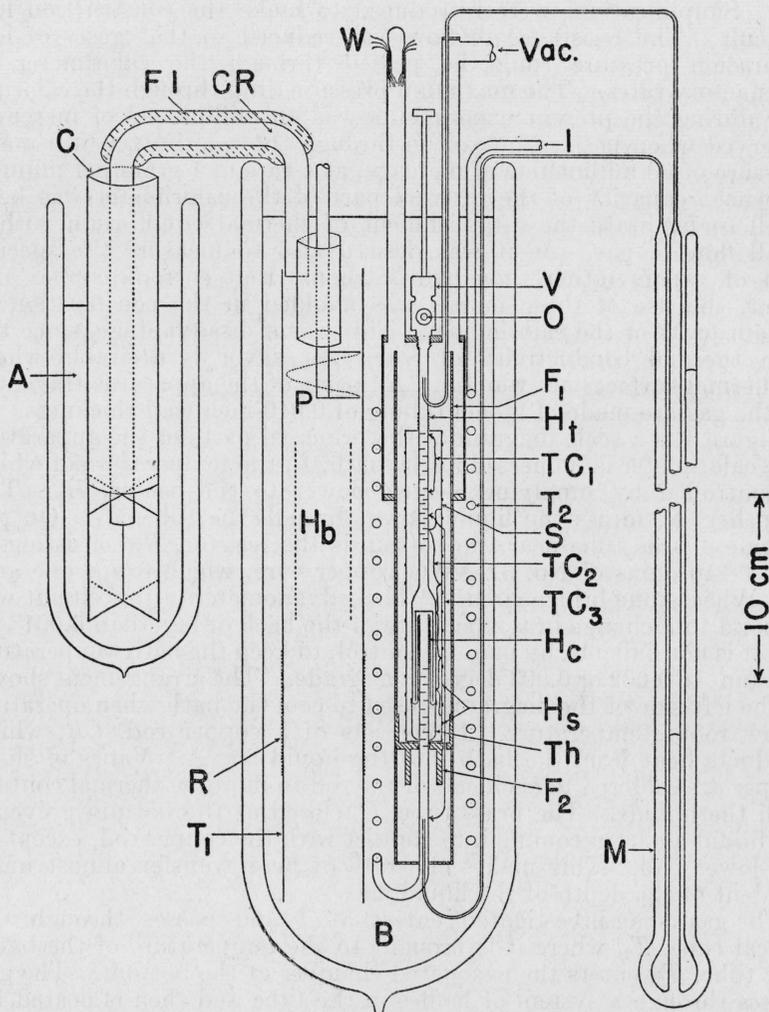

FIGURE 1.—*Scale diagram of calorimeter.*

A, Liquid air; C, protecting cylinder; FI, felt insulation; CR, copper rod; P, propeller; H_b, H_t, H_c, and H_s, electric heaters; R, copper resistor; T_1, stirrer tube; W, wax seal; Vac, vacuum line; I, inlet; V, throttle valve; O, outlet; F_1, flange; TC_1, TC_2, and TC_3, thermocouples; T_2, helical tube; S, radiation shield; Th, metal thimble; F_2, flange; B, constant temperature bath; M, manometer.

The labyrinth which the gas traverses after passing the heater is for the purpose of obtaining an isothermal exterior surface on this part of the calorimeter. The metal thimble, T_h, extends this isothermal surface to a point very close to where the tube enters the

copper radiation shield, S. This shield is heated to the temperature of the inner adjacent wall of the calorimeter by means of the electric heater, H_s, the necessary adjustments being indicated by the three-junction chromel-constantan thermocouple, TC_2. Where the ends of the radiation shield approach to within about one-half millimeter of the tube conducting the gas, metallic contact with the tube is avoided and the shield is supported by a lacing of cotton cord passing through four small holes in each end and around the edges of the center hole.

The rise in temperature of the gas is measured by the five-junction copper-constantan thermocouple TC_3. The wires of this couple make three turns around both the radiation shield and flange F_2 and are cemented with Glyptal lacquer so that they are brought nearly to the correct temperatures before the junctions make thermal contact with the calorimeter tube. The tube heater, H_t, is for the purpose of establishing a zero temperature gradient in the upper part of the tube, the gradient being indicated by the thermocouple, TC_1. All the electrical leads to the heaters and thermocouples enter the vacuum chamber through the wax seal, W, and are brought close to the temperature of the bath by being wound around the flange, F_1.

The pressure of the gas, before and after heating, is measured by means of the manometer, M. The manometer could not be used for the measurements on styrene and ethylbenzene because these materials would have condensed on the surfaces that were at room temperature. During the experiments on these substances the manometer was removed, and the metal connecting tubes were closed by soldering in wires that fit the tubes closely, so that there was very little unoccupied volume in the parts of the tubes, which were at room temperature.

IV. METHOD

The measurements consisted of determinations of the rate of flow, r, of the gas through the calorimeter, the electric power, W, to the calorimeter heater, and the rise in temperature of the gas, Δt. 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 temperature, δt, of gas flowing through the calorimeter, when no power was supplied to the calorimeter heater, H_c. The specific heat of the gas, C_p, at the mean pressure and temperature of the experiment was computed by the relation

$$C_p = \frac{W}{r(\Delta t + \delta t)}.$$

A constant rate of flow of gas was attained by maintaining a constant pressure on the inlet side of the calorimeter and a constant pressure difference between the inlet and outlet. At the start of a measurement the desired rate of flow was obtained by adjusting the throttle valve, V. In the experiments with hydrogen the outlet pressure was atmospheric and the inlet pressure was kept at the desired value above atmospheric by supplying hydrogen from a cylinder through a reducing valve and allowing some of the hydrogen to escape, before entering the calorimeter, by bubbling through a depth of water. In the experiments with the hydrocarbons the inlet pressure was kept constant by controlling the electric power supplied to an external boiler, which

supplied vapor to the inlet of the calorimeter. The outlet pressure was kept very low by condensing the compound in a cold reservoir.

The rate of flow of hydrogen was measured by means of a laboratory wet test gas meter, which could be read to 0.001 cubic foot. This meter was calibrated by the Weights and Measures Division of this Bureau. The hydrogen, before entering the calorimeter, was dried by passing through a cotton filled U-tube cooled with liquid air. After leaving the calorimeter and before entering the gas meter, the hydrogen bubbled through water. This improved the approach to saturation [2] and reduced the amount of water carried out of the meter by the gas. The rates of flow of the hydrocarbons were determined by weighing the amounts collected in the condensing reservoir during measured intervals of time.

The power input to the calorimeter was determined by measuring the current flowing through the heater and the potential drop across the heater. A Wenner potentiometer, together with a volt box and a standard resistor were used for these measurements. The electromotive force of the thermocouple, TC_3, which is used to determine the temperature rise Δt and the Joule-Thomson, δt, was also measured with the Wenner potentiometer. This thermocouple was calibrated, before assembling the calorimeter, by comparison with a standard platinum resistance thermometer.

During the measurements on hydrogen, butadiene, and isobutene, the pressure of the gas, before and after heating, was measured with the manometer, M, (fig. 1). Since the manometer could not be used for measurements on styrene and ethylbenzene it was necessary to calculate the pressures. The ingoing pressure was assumed to be the vapor pressure corresponding to the temperature of the boiler (90° C). The pressure drop in the calorimeter was calculated by means of the relation

$$\Delta p = k\rho V^2,$$

where Δp is the pressure drop, k is a constant, ρ is the density of the gas, and V is the volume rate of flow of gas through the calorimeter. This relation is approximately correct for turbulent flow. The constant, k, was evaluated from measurements on air.

The time required to establish steady conditions, after adjusting the rate of flow and the power input, varied from 20 to 40 minutes, depending upon the rate of flow. After steady conditions were established, measurements of power, temperature rise, and rate of flow were made for periods of from 10 to 30 minutes.

V. TEST OF THE CALORIMETER WITH HYDROGEN

Auxiliary measurements of the specific heat of normal hydrogen were carried out in order to obtain additional information about the accuracy of measurements obtained with this calorimeter. Hydrogen was chosen for this purpose because values of specific heat calculated from spectroscopic data are believed to be trustworthy and there was available an ample supply of material of adequate purity.

Hydrogen was generated electrolytically and stored in a high-pressure cylinder. Earlier analyses of the dried hydrogen prepared in the same way showed an impurity of less than 0.02 mole percent. The

hydrogen was passed through the calorimeter at a pressure slightly above atmospheric. The rates of flow range from 2 to 9 moles per hour for the various measurements. The power input to the calorimeter was usually adjusted to produce a temperature rise of about 10 degrees centigrade although in one case the rise was only 6 degrees. No Joule-Thomson heating was detectable for the rates of flow used in these experiments.

The mean temperatures of the four series of measurements were −29°, 42°, 80°, and 100° C. Upon comparing the observed values with those calculated from spectroscopic data, it appeared that most of the meaured values were a little low and that the discrepancy was greater for small rates of flow. In order to correlate the data for different rates of flow, the differences (in percent) between the observed and spectroscopic values were plotted as ordinates with values of $\Delta t/W$ as abscissas, where Δt is the temperature rise of the gas as it flows through the calorimeter, and W is the power input causing the temperature rise. If the heat lost or gained, because of failure to establish strictly adiabatic conditions, is assumed to be proportional to Δt, $\Delta t/W$ will be proportional to the fractional error in specific heat caused by the loss or gain of heat. For a given gas, if t and Δt are kept constant, $\Delta t/W$ is inversely proportional to the rate of flow. The use of the quantity $\Delta t/W$, rather than the reciprocal of the rate of flow, permits the correlation of data on different materials and with different values of Δt.

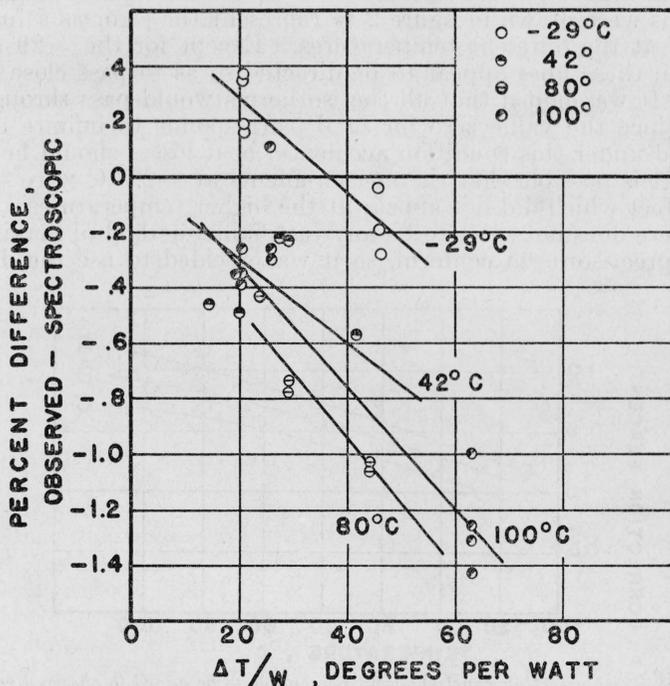
FIGURE 2.—*Results on normal hydrogen.*

Differences, in percent, between observed values of specific heat and those calculated from spectroscopic data, plotted as functions of $\Delta t/W$, the ratio of temperature rise to power input.

Figure 2 shows the correlation for the data on hydrogen. The spectroscopic values of specific heat used are given in table 1. A calculation showed that the difference between the specific heat of hydrogen at 1 atmosphere and in the ideal gas state amounted to only 1 part in 6,000 and hence could be neglected.

TABLE 1.—*Specific heat of normal hydrogen calculated from spectroscopic data* [a]

t	$C°_p$
° C	cal mole⁻¹ deg⁻¹
$°\ C$	$cal\ mole^{-1}\ deg^{-1}$
—29	6. 750
+42	6. 917
+80	6. 955
+100	6. 966

[a] Interpolated from an unpublished table prepared by H. W. Woolley and F. G. Brickwedde.

Although there is a considerable amount of scattering of the individual observations shown in figure 2, it is evident that there is a systematic deviation which depends upon the temperature and upon the value of $\Delta t/W$. Because of the apparent regularity of the deviation, it appeared possible to use the results on hydrogen to apply corrections to the values of specific heat obtained for other gases, although the original purpose of the measurements on hydrogen was to test the accuracy of measurements obtained with this calorimeter. To achieve this result the following correlation was made. The straight line isotherms were drawn in figure 2 to represent the error as a function of $\Delta t/W$ at the different temperatures. Except for the —29 degree isotherm, these lines appear to be directed so as to pass close to the origin. It was hoped that all the isotherms would pass through the origin, since the value zero for $\Delta t/W$ corresponds to infinite rate of flow, and under this condition accidental heat losses should be negligible. It is possible that the measurements at —29° C were subject to an effect which did not appear at the higher temperatures. However, there does not seem to be any justifiable method of making the —29 degree isotherm conform, so it was decided to use the data as
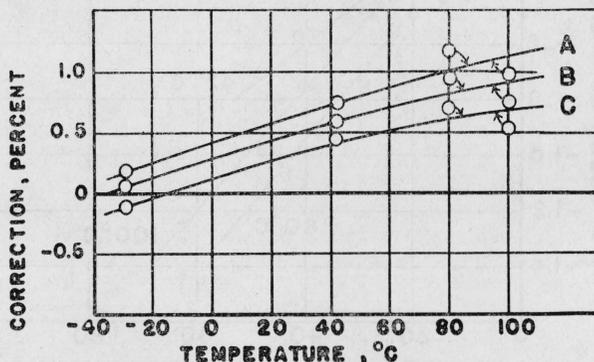

FIGURE 3.—*Correction chart showing percentage to be added to observed values of specific heat*

A, $\Delta t/W=50$ deg per watt; B, $\Delta t/W=40$ deg per watt; C, $\Delta t/W=30$ deg per watt.

they stand. Values of the ordinate (fig. 2) were read off at each temperature for values of $\Delta t/W$ of 30, 40, and 50 degrees per watt. The negatives of these values were plotted as functions of temperature in figure 3, the resulting graph being used for the correction of observations on the other compounds.

VI. RESULTS

Table 2 gives the magnitudes of the quantities observed during the measurements of the specific heats of the hydrocarbons. Also shown are magnitudes of $C_p - C_p{}^\circ$, the difference between the specific heat of the gas at the observed pressure and the specific heat in the ideal state. Values of $C_p - C_p{}^\circ$ were calculated by means of the relation

$$C_p - C_p{}^\circ = \frac{81 R_p T_c{}^3}{32 p_c T^3},$$

in which R is the gas constant, p is the pressure, T is the observed temperature, and T_c and p_c are the critical temperature and pressure, respectively. This relation is derivable from the Berthelot equation of state and the exact thermodynamic relation

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_p.$$

T and T_c are in degrees Kelvin, equal to t° C plus 273.16. The values used for p_c and T_c are given in table 3.

TABLE 2.—*Magnitudes of quantities involved in the determinations of the specific heats of 1,3-butadiene, isobutene, styrene, and ethylbenzene*

| Material | Temperature | Number of observed points | Rate of flow | | Temperature rise, Δt | | Joule-Thomson effect | | Pressure | $C_p - C_p{}^\circ$ |
			Minimum	Maximum	Minimum	Maximum	Minimum	Maximum		
	$^\circ C$		$g\ sec^{-1}$	$g\ sec^{-1}$	$^\circ C$	$^\circ C$	% of Δt	% of Δt	mm Hg	% of C_p
1,3-Butadiene	−35.0	4	0.0085	0.016	9.9	11.6	0.6	2.4	90	0.5
	0.0	5	.013	.024	9.6	9.8	.4	1.3	280	.9
	40.0	5	.015	.021	9.3	9.6	.4	0.8	290	.6
	80.0	4	.008	.021	8.9	9.1	.2	.8	280	.4
Isobutene	−34.0	5	.011	.015	8.4	9.4	1.1	2.1	90	.4
	−1.0	2	.016	.016	8.3	8.3	0.2	0.2	295	.9
	39.0	6	.007	.018	8.7	9.4	.2	.4	290	.5
	80.0	4	.009	.018	7.9	8.1	.1	.6	295	.3
Styrene	100.0	7	.010	.016	10.3	12.3	.6	1.5	125	.3
Ethylbenzene	100.0	7	.008	.020	8.8	10.6	.2	1.5	175	.4

TABLE 3.—*Values of the critical constants used in calculating the values of $C_p - C_p{}^\circ$*

Material	p_c	T_c	Reference
	atm	$^\circ K$	
1,3-Butadiene	42.87	426	Meyers, Scott, Brickwedde, and Rands [3].
Isobutene	39.48	417.9	Beattie, Ingersoll, and Stockmayer [4].
Styrene	36.3	639	Calculated [5].
Ethylbenzene	36.9	619.5	Altschul [6].

Table 4 gives the results of the specific heat measurements on the hydrocarbons. The values given in column 4 are the weighted means of the experimental values, greater weight being given to measurements made with high rates of flow. A correlation similar to that used for the hydrogen data was not satisfactory. In most cases the observed values failed to show a definite trend or dependence on the value of $\Delta t/W$. It seems likely that the trend was masked by the scattering of the individual observations, and that much more data would be required to show a trend in every series of measurements.

Column 5 of table 4 gives the average of the absolute magnitudes of the deviations of the experimental values from the mean value given in column 4. In view of the results on hydrogen it is believed that the values given in column 4 are likely to be low, and that they would be improved by applying the corrections indicated by the hydrogen data. The corrections given in column 7 were obtained from figure 3. The last column shows the corrected values of C_p°, the specific heat in the ideal gas state.

TABLE 4.—*Specific heats in the ideal gas state.*

[Summary of results, including corrections resulting from the test of the calorimeter with hydrogen 1 calorie=4.1833 international joules.]

Material	Temper- ature	Number of obser- vations	$C_p - C_p^\circ$	C_p° weighted mean	ΔC_p° average devia- tion from weighted mean	$\Delta t/W$	Correc- tion	C_p° corrected
	°C		cal mole⁻¹ deg⁻¹	cal mole⁻¹ deg⁻¹	cal mole⁻¹ deg⁻¹	deg watt⁻¹	%	cal mole deg⁻¹
Butadiene	−35.0	4	0.08	15.72	0.04	50	0.13	15.74
	0.0	5	.16	17.64	.04	30	.12	17.66
	40.0	5	.11	19.95	.03	30	.41	20.03
	80.0	4	.08	22.11	.03	30	.62	22.25
Isobutene	−34.0	5	.08	18.10	.08	50	.14	18.13
	−1.0	2	.18	19.76	.01	40	.27	19.81
	39.0	6	.12	21.78	.03	40	.58	21.91
	80.0	4	.08	23.76	.03	40	.84	23.96
Styrene	100.0	7	.11	35.83	.07	40	.92	36.16
Ethylbenzene	100.0	6	.16	37.71	.07	40	.92	38.06

VII. ESTIMATE OF ACCURACY

The only reliable evidence concerning the accuracy of the results is contained in the measurements of the specific heat of hydrogen. If the individual observations on hydrogen had been simply averaged at each temperature, the greatest difference between the observed mean values and the spectroscopic values would have been 0.8 percent. Although the values obtained for the hydrocarbons were corrected by making use of the data on hydrogen, it is too optimistic to assume that the systematic error was entirely eliminated, since it has not been proved that the error is independent of the nature of the gas being investigated. However, it is reasonable to expect that making the corrections resulted in some improvement. Therefore, it is the authors' opinion that errors in the corrected values given in table 4 are probably less than 0.5 percent.

VIII. COMPARISON WITH WORK OF OTHER OBSERVERS

While this paper was being prepared for publication two articles appeared that reported measurements of the specific heat of butadiene vapor. In the first of these papers, by Aston, Moessen, Hardy, and Szasz [7], the specific heats were computed from measurements of the velocity of ultrasound. The second paper, by Templeton, Davies, and Felsing [8], reported calorimetric measurements. Figure 4 shows the data of the different observers. A line was drawn through the data
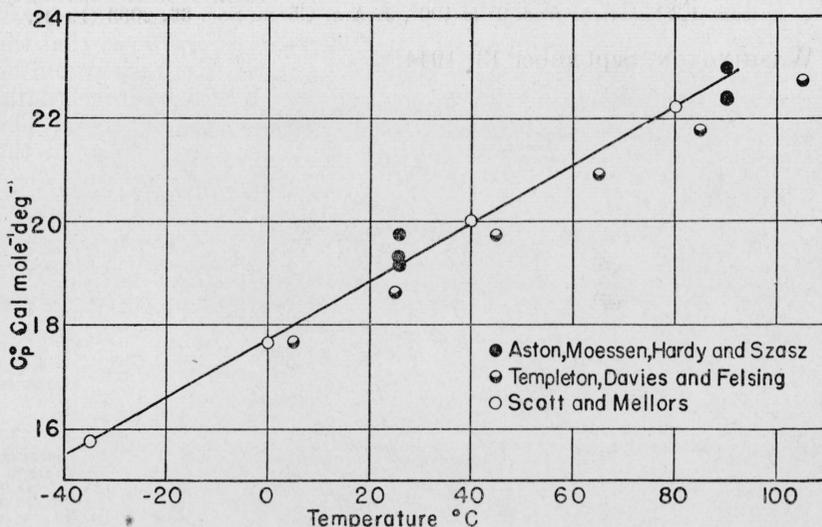

FIGURE 4.—*Specific heat of 1,3-butadiene vapor.*

Comparison of values obtained by different observers. The solid circles showing the data of Aston, Moessen, Hardy, and Szasz do not represent three separate determinations at each temperature, but result from three different methods of computing specific heats from a single series of experimental data at each temperature.

of the present investigation in order to facilitate comparison at intermediate temperatures. The solid circles on the graph showing the data of Aston, Moessen, Hardy, and Szasz do not represent three separate determinations at each temperature, but result from three different methods of computing specific heats from a single series of experimental data at each temperature. The data of Templeton, Davies, and Felsing are systematically lower than those obtained in the present work, the maximum difference amounting to about 3 percent. This difference is larger than would be expected from a consideration of the estimated errors, since Templeton, Davies, and Felsing estimate their over-all accuracy as better than 1 percent.

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