

- $R$  = universal gas content, (lb.) cu. ft./ (sq. in.) (lb.-mole) ( $^{\circ}\text{R.}$ )  
 $T$  = temperature,  $^{\circ}\text{R.}$   
 $x$  = mole fraction  
 $\alpha$  = BWR equation of state coefficients  
 $\gamma$  = BWR equation of state coefficients

#### Subscripts

- $i$  = component  $i$   
 $m$  = mixture property  
 $1, 2$  = components 1 and 2

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# The Constant-Volume Heat Capacities of Gaseous Perfluorocyclobutane and Propylene

NOEL DE NEVERS and JOSEPH J. MARTIN

University of Michigan, Ann Arbor, Michigan

The constant-volume heat capacities of gaseous perfluorocyclobutane and propylene have been measured over a considerable range of temperatures and densities with a new type of adiabatic calorimeter. This calorimeter differs from previous constant-volume gas calorimeters in having very thin walls and being equipped with an internal motor stirrer to provide temperature uniformity. The experimental results have been compared with the predictions of the Benedict-Webb-Rubin and Martin-Hou equations, by use of published values of the zero-pressure-constant-volume heat capacity. The over-all agreement is satisfactory, with a maximum difference between the experimental and calculated heat capacities of 6.7%; however the comparison reveals several interesting, systematic differences between the experimental and calculated values of the derivatives of the constant-volume heat capacity with respect to temperature and density.

Although the constant-volume heat capacity has been less intensively investigated than the constant-pressure heat capacity, it is just as useful in thermodynamic calculations as  $C_p$ . At zero pressure the two are related by the equation  $C_v^* = C_p^* - R$ . At finite pressures  $C_v$  and  $C_p$  may be computed from the corresponding zero-pressure values and PVT data as represented by an equation of state by use of the relations

$$C_v - C_v^* = - \int_v^{\infty} T \left( \frac{d^2P}{dT^2} \right)_v dV_T \quad (1)$$

$$C_p - C_p^* = - \int_0^P T \left( \frac{d^2V}{dT^2} \right)_P dP_T \quad (2)$$

(Although in principle the necessary second derivatives can be computed directly from PVT data, in practice such data are rarely available in such quantity and precision that the second derivatives can be calculated without recourse to a numerical equation of state or a graphical one, for example a compressibility plot.)

Comparison of the experimental values of  $C_v - C_v^*$  or  $C_p - C_p^*$  with those calculated by Equations (1) and (2) is a very sensitive test of the accuracy of an equation of state. Inspection of Equations (1) and (2) reveals that  $C_v - C_v^*$  is readily calculated by means of a pressure-explicit equation of state,  $P = f(V, T)$ , and that  $C_p - C_p^*$  is readily calculated by means of a volume-explicit equation  $V = f(P, T)$ . Computation of  $C_v - C_v^*$  from a volume-explicit equation or of  $C_p - C_p^*$  from a pressure-explicit equation is

possible but awkward. Most currently used equations are pressure-explicit, for example the Beattie-Bridgeman (1), Benedict-Webb-Rubin (2), and Martin-Hou (14) equations; the accuracy of these equations can be tested and possible improvements suggested by  $C_v - C_v^*$  data, but such tests cannot be conveniently made with  $C_p - C_p^*$  data. Furthermore  $C_p$  increases without limit near the critical state, whereas  $C_v$  does not; so  $C_v$  may be used to check state data near the critical point but  $C_p$  may not.

The major experimental problems of  $C_p$  calorimetry have long been solved (17);  $C_v$  calorimetry presents a different set of experimental problems, which have not yet been completely overcome. Measurements of  $C_p$  are performed in a flow calorimeter at steady state. As the temperature of the apparatus does not change with respect to time, the heat capacity of the calorimeter does not enter the calculations of  $C_p$ . Measurements of  $C_v$ , however, are performed in an unsteady state by heating a known mass of gas plus its container through a measured temperature interval. The heat capacity of the container must be subtracted from the measured heat capacity to compute the

Noel De Nevers is with California Research Corporation, Richmond, California.

heat capacity of the contents. In previous  $C_v$  calorimetry (3, 4, 5, 7, 10, 11, 19, 21) the heat capacity of the calorimeter has been up to twenty times that of its contents; under these circumstances a small error in the measured heat capacity corresponds to a large error in the heat capacity of the contents. Michels and Strijland (19) using a differential calorimeter measured the  $C_v$  of carbon dioxide with fair precision. Theirs has been the only work to date which shows  $C_v$  over a wide range of temperature and density for any compound.

In this research a new type of calorimeter was used. In principle the calorimeter was the simple adiabatic type; the experimental substance was contained in the calorimeter, which was placed in an evacuated space and surrounded by a shield whose temperature was maintained as close as possible to that of the calorimeter. Measured amounts of heat were added to the calorimeter and its contents, and from the measured temperature rise the heat capacity of the aggregate was computed. The calibrated heat capacity of the calorimeter was subtracted from the heat capacity of the aggregate to find the heat capacity of the contents. This calorimeter was novel in two respects. First, it was very thin-walled. Being designed to operate in the pressure range of 200 to 900 lb./sq. in. and to burst at a pressure of 1,000 lb./sq. in., it had a heat capacity much lower than that of a comparable calorimeter designed with a normal safety factor; naturally it was necessary to provide shielding to limit the destructive effects of rupture of the calorimeter. Second, this calorimeter had an internal, electric motor stirrer to provide temperature uniformity. The several constant-volume calorimeters of Sage *et al.* (4) have used internal stirring, dependent on external motors; all other previous  $C_v$  calorimeters have depended on natural convection and conduction of heat through their thick metal walls to provide temperature

uniformity. The internal motor stirrer was chosen in preference to an external one because it was simple (no shaft seals or magnetic coupling), because it made calculation of the stirring energy input simple (all the electrical energy used by the motor entered the gas as motor heat loss or as stirring energy), and because it eliminated the problem of heat conduction along the stirrer shaft or magnetic coupling shaft.

## EXPERIMENTAL APPARATUS AND MATERIALS

The calorimeter proper was a sphere of type-304 extra-low-carbon stainless steel, 8.015 in. I.D. and with a wall thickness of 0.031 in. Inside it were a platinum coil, which served both as a heater and as a platinum-resistance thermometer, and a 12-volt D.C. motor which drove a 2½-in. propeller. The electrical leads to these instruments left the calorimeter through kovarglass lead seals, silver-soldered into the wall of the calorimeter. A small needle valve, also silver-soldered into the wall of the calorimeter was used for loading and unloading the calorimeter. Figure 1 shows the lower half of the calorimeter before assembly; on it the thermometer heater and motor are visible. The two cold-drawn halves of the calorimeter were joined by Heliarc fusion welding, and the outside of the calorimeter was copper-plated to reduce its emissivity for radiant heat transfer. Figure 2 is a cross section of the calorimeter assembly, showing the calorimeter, adiabatic shield, and vacuum container.

The calorimeter was supported in place by three Fiberglass strings. Surrounding it was an adiabatic shield in the form of a cubical box made of six copper plates,

each 10 in. square and ¼ in. thick. The inside surfaces of the shield were coated with aluminum foil to reduce radiant heat transfer. Electric heaters attached to the outside of the shield were used to control its temperature. Three differential thermocouples measured the differences in temperature between the top, side, and bottom of the calorimeter and corresponding points on the adiabatic shield.

The shield was supported within a steel vacuum container, which was designed to contain the experimental substance and any fragments in case of a rupture of the calorimeter. It was constructed of ¼-in.-thick mild steel and had a removable top, retained by 8½-in. bolts, with a silicone-rubber gasket making a vacuum seal at the top. A vacuum pump was used to evacuate the container and to provide the necessary vacuum for loading and unloading the calorimeter. The container was covered with Fiberglass insulation to reduce heat leakage to the surroundings. The electrical leads to the calorimeter and to the differential thermocouples left the vacuum system through a vacuum junction box placed several feet from the vacuum container in order to prevent thermal electromotive forces from forming in the soldered junctions.

During heating periods the current input to the calorimeter passed through the motor and thermometer heater in series. About three quarters of the power was dissipated by the thermometer heater and the remainder by the motor. The current through the thermometer heater and motor was determined by measuring the voltage across a standard resistor in series with them; the voltage across the thermometer heater and motor was determined by measuring the voltage across a standard resistor in a circuit parallel to them. A balancing resistor (9) in series with the

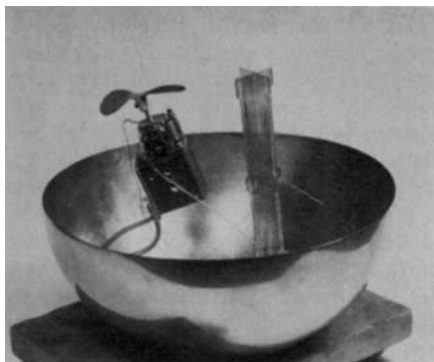


Fig. 1. View of lower half of the unassembled calorimeter.

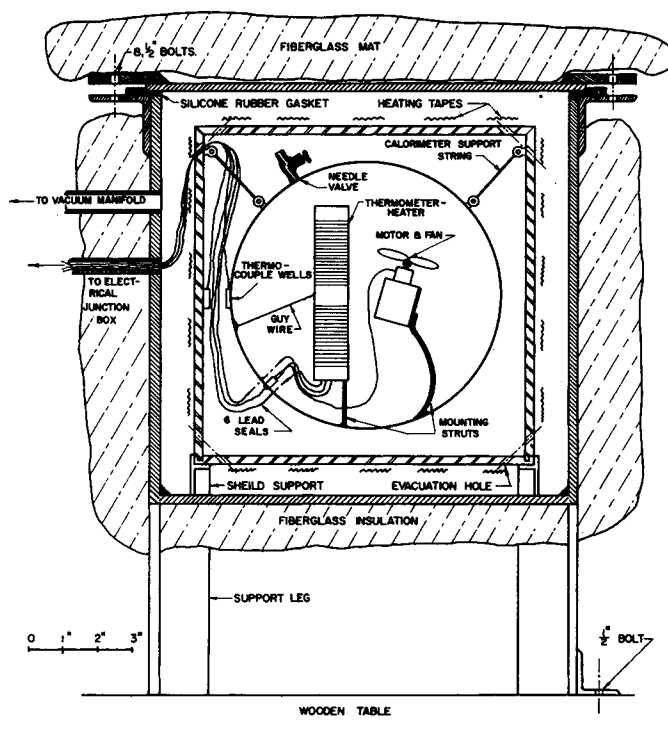


Fig. 2. Cross section of the calorimeter assembly.

TABLE 1. THE CONSTANT-VOLUME HEAT CAPACITY OF PERFLUOROCYCLOBUTANE

| Density, g./cc. | $T_{mean}$ , °C. | Heat capacity, cal./ (g.) (°C.) |
|-----------------|------------------|---------------------------------|
| 0.1569          | 101.58           | 0.2117                          |
|                 | 103.45           | 0.2164                          |
|                 | 114.99           | 0.2190                          |
|                 | 126.33           | 0.2212                          |
|                 | 137.41           | 0.2243                          |
|                 | 146.61           | 0.2250                          |
| 0.1927          | 109.18           | 0.2204                          |
|                 | 119.24           | 0.2237                          |
|                 | 131.73           | 0.2257                          |
|                 | 144.05           | 0.2277                          |
| 0.2394          | 110.50           | 0.2272                          |
|                 | 118.11           | 0.2269                          |
|                 | 127.20           | 0.2279                          |
|                 | 136.20           | 0.2287                          |
|                 | 145.10           | 0.2301                          |
| 0.3201          | 117.32           | 0.2357                          |
|                 | 126.40           | 0.2339                          |
|                 | 135.43           | 0.2356                          |
|                 | 144.40           | 0.2341                          |
| 0.3902          | 114.67           | 0.2482                          |
|                 | 118.37           | 0.2436                          |
|                 | 124.01           | 0.2393                          |
|                 | 131.58           | 0.2377                          |
|                 | 139.12           | 0.2373                          |
|                 | 146.69           | 0.2374                          |
| 0.4465          | 119.27           | 0.2492                          |
|                 | 123.01           | 0.2445                          |
|                 | 127.74           | 0.2416                          |
|                 | 134.37           | 0.2398                          |
|                 | 141.97           | 0.2388                          |
| 0.5366          | 147.66           | 0.2390                          |
|                 | 119.04           | 0.2594                          |
|                 | 123.56           | 0.2498                          |
|                 | 129.42           | 0.2445                          |
|                 | 136.16           | 0.2417                          |
|                 | 142.95           | 0.2400                          |

heater and motor minimized the changes in heater power that occurred with changes in thermometer-heater and motor resistance. The temperature of the calorimeter was determined from the resistance of the thermometer heater. (This measurement was never made while current was flowing through the thermometer heater and motor.) Elapsed time of a heating period was measured with a synchronous timer, whose clutch was actuated by the switch which controlled the power to the calorimeter.

The perfluorocyclobutane was stated to be 99.78 weight % pure; the propylene was C.P. grade, specified to be 99.0 mole % pure. Neither of these materials was subjected to any additional purification.

#### EXPERIMENTAL PROCEDURE

The material to be investigated was placed in a light-weight stainless steel transfer container, which was weighed, and then an amount of substance was transferred to the calorimeter by vacuum transfer methods. The transfer container was reweighed and the calorimeter loading thus determined. For this operation and for unloading, the top of the vacuum container and the top member of the adiabatic shield were removed and the calorimeter was suspended from a crane above the vacuum container. When loading was

complete, the calorimeter was lowered into place, the adiabatic shield and vacuum container were reassembled, and the sys-

tem was evacuated (normally to about 0.050 mm. Hg).

When the calorimeter had been heated

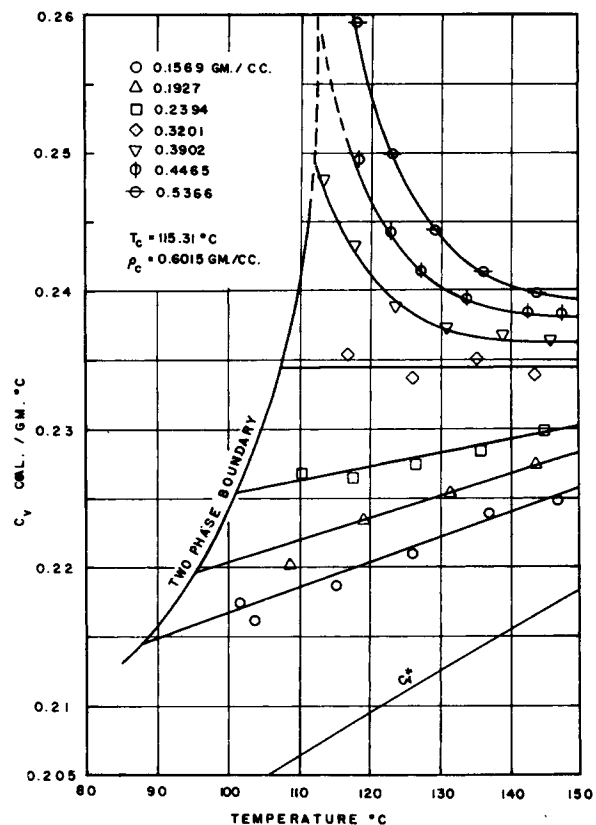


Fig. 3. Constant-volume heat capacity of perfluorocyclobutane.

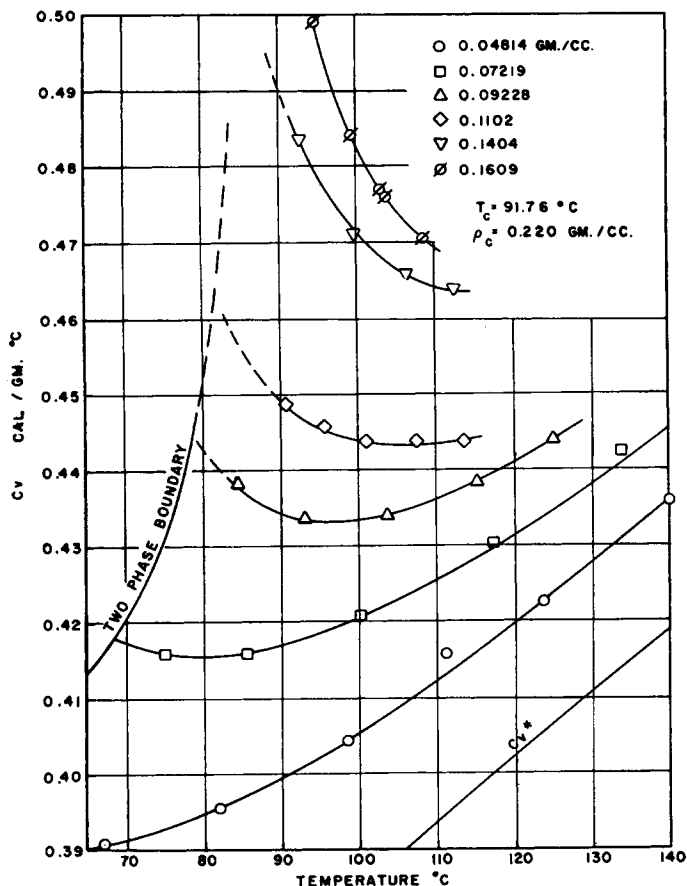


Fig. 4. Constant-volume heat capacity of propylene.

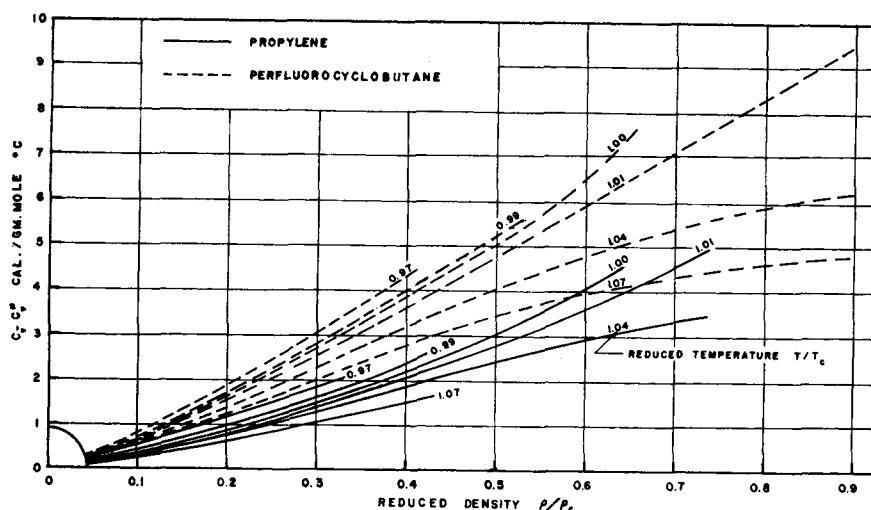


Fig. 5.  $C_v - C_v^*$  as a function of reduced temperature and reduced density.

to the desired starting temperature, the shield was controlled to maintain zero average temperature differences between the control points on the surfaces of the calorimeter and the shield. The temperature was measured at 5 min. intervals until its rate of change with respect to time or "drift" had been determined. (This drift was normally about 0.002°C./min.) Then the power was switched to the thermometer heater and motor. At times corresponding to one quarter, one half, and three quarters of the heating period the power input to the thermometer heater and motor was measured, and the average of these three power readings was used in subsequent calculations. Heating periods were of 15-, 20-, 25-, 30- and 40-min. duration, depending on the desired tem-

perature change. At the end of the heating period the power was switched away from the calorimeter. The temperature was again measured at 5-min. intervals until the drift had been determined. This drift was used to extrapolate the temperature-time curve to the time of power shut-off. If only one measurement was planned, operations ceased after this drift had been found; if several measurements were planned, a new heating period was begun as soon as this drift had been determined. When the heat capacity had been measured over the planned temperature range, the calorimeter was cooled and unloaded by methods similar to the loading procedure. The difference between the measured load and the quantity of material recovered seldom exceeded 0.1% of the load.

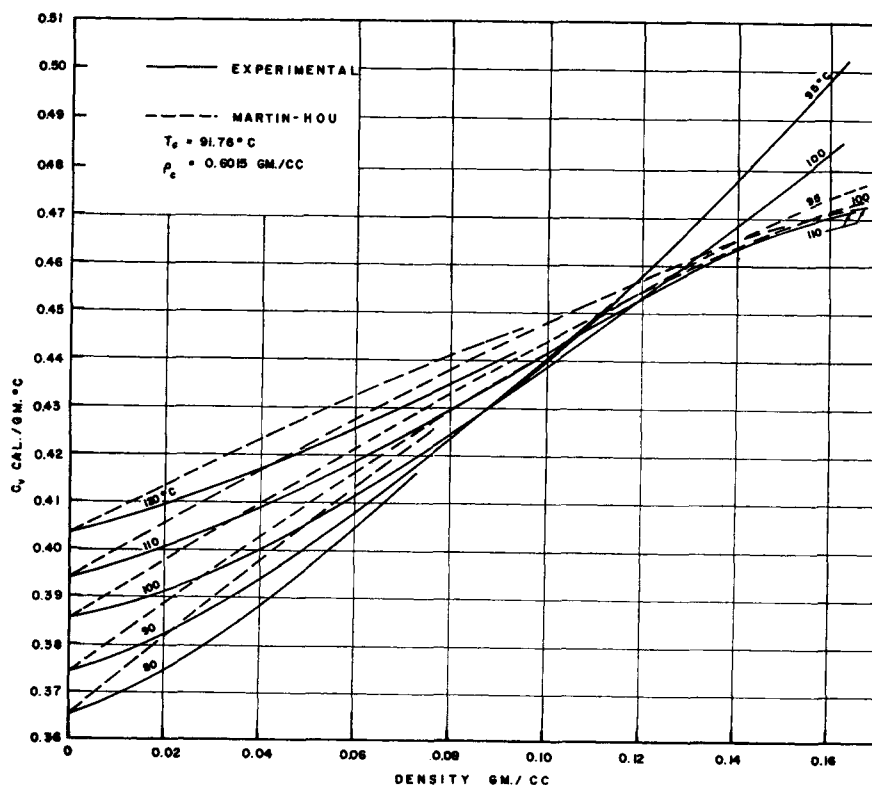


Fig. 6. Comparison of the experimental  $C_v$  of propylene with the  $C_v$  predicted by the Martin-Hou equation.

TABLE 2. THE CONSTANT-VOLUME HEAT CAPACITY OF PROPYLENE

| Density, g./cc. | $T_{mean}$ , °C. | Heat capacity, cal./ (g.) (°C.) |
|-----------------|------------------|---------------------------------|
| 0.04814         | 67.15            | 0.3903                          |
|                 | 82.14            | 0.3952                          |
|                 | 98.45            | 0.4047                          |
|                 | 111.62           | 0.4159                          |
|                 | 123.90           | 0.4226                          |
|                 | 140.21           | 0.4357                          |
| 0.07219         | 75.09            | 0.4160                          |
|                 | 85.21            | 0.4163                          |
|                 | 99.93            | 0.4208                          |
|                 | 117.06           | 0.4305                          |
|                 | 133.72           | 0.4412                          |
|                 | 145.92           | 0.4485                          |
| 0.09228         | 84.64            | 0.4380                          |
|                 | 92.91            | 0.4337                          |
|                 | 103.71           | 0.4341                          |
|                 | 115.35           | 0.4385                          |
|                 | 125.32           | 0.4439                          |
| 0.1102          | 90.71            | 0.4486                          |
|                 | 95.75            | 0.4460                          |
|                 | 101.28           | 0.4438                          |
|                 | 107.59           | 0.4439                          |
|                 | 113.37           | 0.4438                          |
| 0.1404          | 93.17            | 0.4842                          |
|                 | 99.58            | 0.4710                          |
|                 | 106.68           | 0.4659                          |
|                 | 112.47           | 0.4638                          |
| 0.1609          | 94.92            | 0.4991                          |
|                 | 99.51            | 0.4840                          |
|                 | 104.51           | 0.4761                          |
|                 | 103.74           | 0.4768                          |
|                 | 108.41           | 0.4704                          |

All the data reported in this paper were collected at calculated pressures less than 800 lb./sq. in. An attempt was made to make a final measurement on propylene in the pressure range of 800 to 900 lb./sq. in.; however during this measurement the calorimeter ruptured at a pressure estimated to be about 860 lb./sq. in. The vacuum container had been designed to contain the propylene in case the thin-walled sphere leaked, but the sphere split in half along the weld almost instantly, blowing the top off the vacuum container. The propylene rushed out, mixed with the air, and exploded. A new container—cylindrical instead of cubical—is being constructed with better safety features.

## CALCULATIONS

The gross heat capacity  $C_g$  of the calorimeter plus contents was determined at the mean temperature of a given experiment by the equation

$$C_g = q_{mean} \Delta\theta / (\Delta T - \Delta T_{corr}) \quad (3)$$

$\Delta T_{corr}$  was that change in temperature which would have occurred in time  $\Delta\theta$  if no energy had been added electrically. It was computed from the drift before the heating period, drift<sub>1</sub>, and the one after, drift<sub>2</sub>, by

$$\Delta T_{corr} = \Delta\theta(\text{drift}_1 + \text{drift}_2)/2 \quad (4)$$

Equation (3) assumes that the gross heat capacity varies linearly with respect to temperature and that the

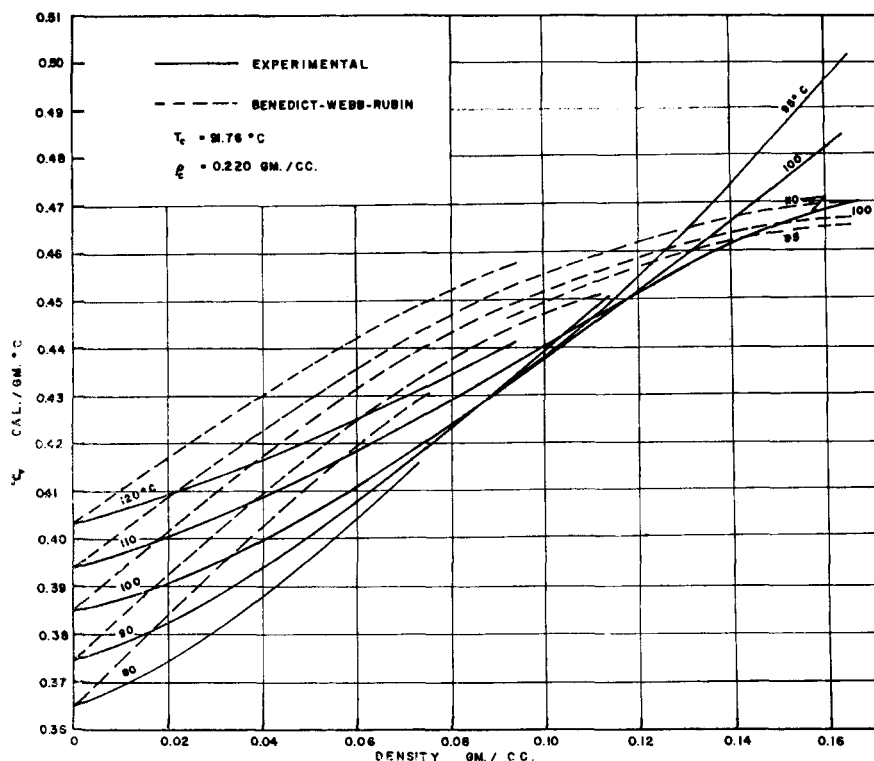


Fig. 7. Comparison of the experimental  $C_v$  of propylene with the  $C_v$  predicted by the Benedict-Webb-Rubin equation.

mean power varies linearly with time. The error introduced by these assumptions is negligible.

The estimated maximum uncertainty in  $C_v$  due to the uncertainties in the various measurements is  $q_{mean}$ , 0.3%;  $\Delta\theta$ , negligible;  $\Delta T$ , 0.3% and  $\Delta T_{corr}$ , 0.2%. Thus the maximum uncertainty in  $C_v$  if these uncertainties had had the same sign would have been 0.8%. If an error of 0.8% had been made in one direction in the calibration and in the other direction in the heat-capacity measurements, this would have led to an error in  $C_v$  of 1.1% at the highest density used and of 3.2% at the lowest. The internal consistency of the data (maximum scatter of 0.7%, average scatter of less than 0.3%) indicates that the uncertainties were random in direction and thus that the accuracy of the data is much better than the above maxima. The maximum error in density was estimated to be 0.3%.

#### CALIBRATION

The heat capacity of the calorimeter as a function of temperature was determined by filling the calorimeter with materials of known heat capacities, measuring  $C_p$ , and subtracting the heat capacities of the contents according to

$$\text{calibration} = C_p - MC_v^* - M(C_v - C_v^*) \quad (5)$$

Two calibration substances were used, propylene and dichlorodifluoromethane (Freon 12). The values of  $C_v^*$  used for

propylene were those given by Kilpatrick and Pitzer (12); for dichlorodifluoromethane those of Masi (18) were used. The values of  $C_v - C_v^*$  used were calculated by the Martin-Hou equation, from constants presented in (13) and (14). For none of the calibration values did the value of  $MC_v^*$  exceed 7% of the value of  $C_p$ , nor did the value of  $M(C_v - C_v^*)$  ex-

ceed 0.1% of  $C_p$ . The maximum scatter of the calibration points from the curve drawn through them was 0.8%, and the average was 0.4%.

#### THE CONSTANT-VOLUME HEAT CAPACITY OF PERFLUOROCYCLOBUTANE

The constant-volume-heat-capacity results for perfluorocyclobutane are shown in Table 1. Seven densities were used ranging from 0.1569 (26.2% of the critical density) to 0.5366 g./cc. (89.6% of the critical density). The temperature range for each density was from the saturation temperature to 150°C. The measured heat capacity over this temperature and density range varies from 0.2164 to 0.2594 cal./g. (°C.). These data are shown in Figure 3 on a  $C_v$ -vs.-temperature plane; a smooth curve has been drawn through the individual points for each density. Also shown on Figure 3 are the boundary of the two-phase region calculated from the PVT data, the values of  $C_v^*$ , and the critical temperature and density reported by Martin *et al.* (15).

#### THE CONSTANT-VOLUME HEAT CAPACITY OF PROPYLENE

Table 2 shows the constant-volume-heat-capacity results for propylene. Six densities were used, ranging from 0.04814 (21.8% of the critical density) to 0.1609 g./cc (72.6% of the critical density). There is some question about the value of the critical density of propylene; throughout this paper

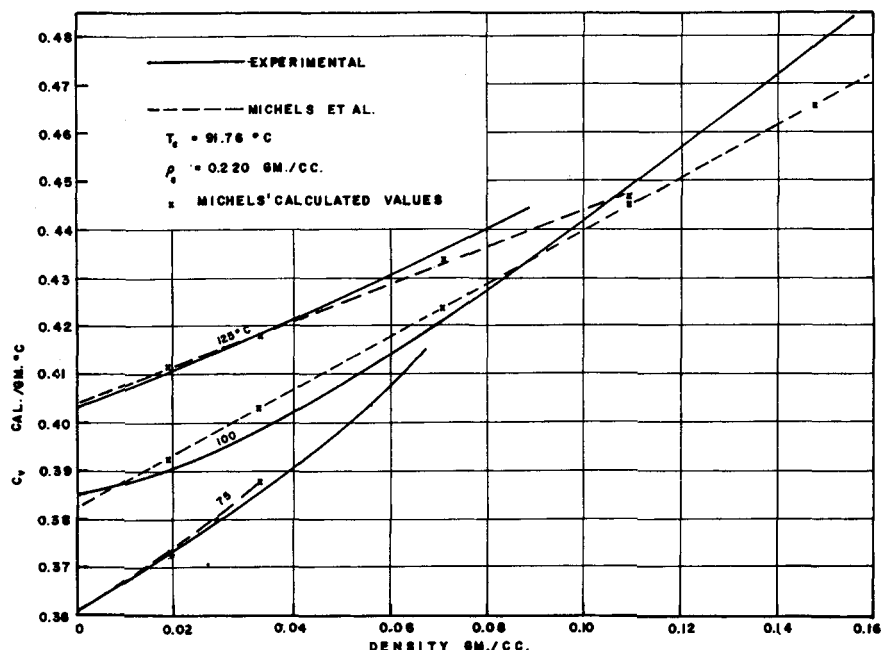


Fig. 8. Comparison of the experimental  $C_v$  of propylene with the calculated  $C_v$  according to Michels *et al.*

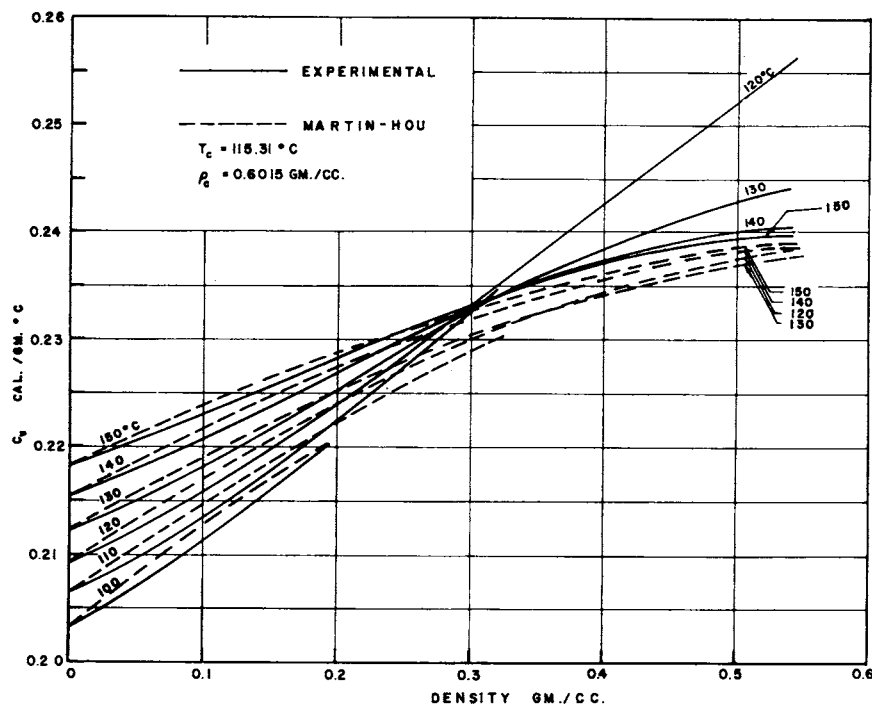


Fig. 9. Comparison of the experimental  $C_v$  of perfluorocyclobutane with the  $C_v$  predicted by the Martin-Hou equation.

the value of 0.220 g./cc. reported by Marchman, Prengle, and Motard (16) has been used. Farrington and Sage (8) report a value of 0.230 g./cc., which seems more reasonable in comparison with other compounds. The temperature range for the two lowest densities was from the saturation tem-

responding states (6), which says that the compressibility factor ( $Z = PV/RT$ ) is the same function of reduced temperature and reduced density for all gases, the molar value of  $C_v - C_v^*$  must be the same for all gases at the same reduced temperature and reduced density:

$$C_v - C_v^* = -RT_R \int_0^{\rho_R} \left[ \frac{T_R}{\rho_R} \left( \frac{d^2 Z}{dT_R^2} \right) + \frac{2}{\rho_R} \left( \frac{dZ}{dT_R} \right) \right] d\rho_R \quad (6)$$

perature to 150°C.; for the two intermediate densities, from the saturation temperature to that temperature at which the calculated pressure was 700 lb./sq. in.; for the two highest densities, from the saturation temperature to that temperature at which the calculated pressure was 800 lb./sq. in. Over this range of temperatures and densities the measured  $C_v$  varies from 0.3903 to 0.4991 cal./g. (°C). These data are shown in Figure 4 on a  $C_v$ -vs.-temperature plane. Also shown on this figure are the values of the critical temperature and the critical density, the boundary of the two-phase region calculated from the PVT data of Marchman *et al.* (16), and the values of  $C_v^*$  reported by Kilpatrick and Pitzer (12).

## DISCUSSION

Several interesting features of the data are revealed by Figure 5, which is a modified cross plot of Figures 3 and 4. On it, for equal reduced temperatures, isotherms for both compounds have been constructed on a molar  $C_v - C_v^*$ -vs.-reduced-density plane. According to the law of cor-

responding states (6), which says that the compressibility factor ( $Z = PV/RT$ ) is the same function of reduced temperature and reduced density for all gases, the molar value of  $C_v - C_v^*$  must be the same for all gases at the same reduced temperature and reduced density:

$$\left( \frac{d^2 C_v}{d\rho^2} \right) = \frac{d}{d\rho_T} \left[ \frac{-T}{\rho^2} \left( \frac{d^2 P}{dT^2} \right) \right] = T \left[ \frac{2}{\rho^3} \left( \frac{d^2 P}{dT^2} \right) - \frac{1}{\rho^2} \left( \frac{d^3 P}{dT^2 d\rho_T} \right) \right] \quad (7)$$

approximate generalizations of PVT data, it is not sufficiently accurate to generalize  $C_v - C_v^*$  data. The reason for this is apparent from Equation (6); an error of several per cent in  $Z$  is made by assuming that perfluorocyclobutane and propylene have the same  $Z = f(T_R, \rho_R)$ , and the two differentiations and one integration in Equation (6) greatly magnify this error.

As noted above, comparison of  $C_v$  data over a range of temperatures and densities with  $C_v$  calculated from  $C_v^*$  and an equation of state is a very sensitive test of a pressure-explicit equation of state. The measured  $C_v$  values

of perfluorocyclobutane have been compared with the  $C_v$  predicted by the Martin-Hou equation, by use of the constants and values of  $C_v^*$  presented by Martin *et al.* (15). The measured  $C_v$  values of propylene have been compared with the predictions of the Martin-Hou equation by use of the constants presented by Martin and Hou (14) and the  $C_v^*$  values of Kilpatrick and Pitzer (12). They have also been compared with the predictions of the Benedict-Webb-Rubin equation through the constants presented by Marchman *et al.* (16) and the above  $C_v^*$  values; finally they have been compared with the  $C_v$  values calculated from PVT data by Michels *et al.* (20). [Michels *et al.* used the  $C_v^*$  values of Stull and Mayfield (22), which differ slightly from those mentioned above.] The comparisons for propylene are shown in Figures 6, 7, and 8, and the the comparison for perfluorocyclobutane is shown in Figure 9.

In general the agreement is good; the maximum difference between the experimental and calculated values in any of the above comparisons is 6.7% of  $C_v$ . This maximum occurred between the experimental and calculated values of  $C_v$  for perfluorocyclobutane at 89.6% of the critical density and 4.67°C. above the critical temperature. Further from the critical state the agreement is much better. However the comparison reveals the following systematic differences between the experimental data and the predictions of the equations of state.

1. The experimental isotherms on a  $C_v$ -vs.-density plane (or a  $C_v - C_v^*$ -vs.-density plane) curve upward at low densities. (If the lowest density  $C_v$  values were extrapolated linearly to zero density, errors of 1 to 4% in  $C_v^*$  would result.) Mathematically this means that

is positive at low densities. This upward curvature decreases with increasing temperature. The Beattie-Bridgeman equation predicts that Equation (7) is positive at low densities, while the Martin-Hou and Benedict-Webb-Rubin equations predict that it is negative.\* For this reason both the latter

\* An improved form in the Martin-Hou equation has been developed and will be published soon. In the improved form the  $C_v$  constant, which was previously zero, has a finite positive value, and the  $C_3$  constant, which was previously positive, is negative. The values of  $A_2, B_2, A_4, A_5, B_5$ , and  $C_5$  are changed slightly, but their signs are not changed. This improved version makes  $[(d^2 C_v)/(d\rho^2)]_T$  positive at low densities.

equations predict  $C_v$  values which are too high in the density range from zero to about one-quarter the critical density as seen in Figures 6, 7, and 9. Michels *et al.* (20) do not present formulas for the calculation of  $C_v$ , but only tabulated values of the 75°, 100°, and 125°C isotherms. These tabulated values show that the 75°C isotherm curves upward slightly more than the experimental isotherm, while the 100° and 125°C isotherms are almost exactly straight, as is shown in Figure 8.

2. The experimental isotherms are straight or nearly straight in the density range of one-quarter to one-half the critical density; that is, Equation (7) is zero or very small in this region. The Beattie-Bridgeman equation has a zero value of Equation (7) at one point in this region, and the Benedict-Webb-Rubin and Martin-Hou equations predict that it is negative throughout the region. According to the isotherms of Michels *et al.*, Equation (7) is zero throughout this region.

3. The experimental data show that for densities greater than one-half of the critical density the isotherms for temperatures near the critical temperature are straight or curve upward, but those at higher temperatures curve downward; that is, Equation (7) is zero or positive for low temperatures and negative for higher temperatures. All three of the above equations represent  $C_v - C_v^*$  as the product of a function of temperature and a function of density:

$$C_v - C_v^* = f(T) \cdot f(\rho) \quad (8)$$

Thus these equations predict that the isotherms on a  $C_v - C_v^*$ -vs.-density plane will be similar; that is, given one isotherm it will be possible to construct any other isotherm by multiplying the ordinates of the first isotherm by a constant multiplier. In particular these equations predict that Equation (7) must have the same sign for all temperatures at a given density, since  $f(T)$  is always positive in these equations. Thus the above equations cannot accurately represent both the high- and low-temperature isotherms over the density range of the data. In order to represent accurately all the  $C_v$  data, an equation which predicts a more complicated  $C_v - C_v^*$  function will be necessary.

4. At densities greater than one-half of the critical density  $C_v$  decreases with increasing temperature; that is,  $(dC_v/dT)_\rho$  is negative, as shown in Figures 3, 4, 6, and 7. From Figures 6 and 7 it is seen that for propylene the Martin-Hou equation predicts this behavior qualitatively but does not predict  $(dC_v/dT)_\rho$  accurately and that the Benedict-Webb-Rubin equation predicts that  $(dC_v/dT)_\rho$  is positive over the en-

tire range of the data. For perfluorocyclobutane the Martin-Hou equation predicts that  $(dC_v/dT)_\rho$  is negative for temperatures below 130°C. and positive for higher temperatures. Because the Beattie-Bridgeman equation uses the same  $f(T)$  in Equation (8) as the Benedict-Webb-Rubin equation, their predictions of  $(dC_v/dT)_\rho$  at these densities should be similar.

5. The measured  $C_v$  increases very rapidly with decreasing temperatures at high densities and temperatures close to the saturation temperature. Michels and Strijland (19) observed similar behavior in their measurements on carbon dioxide, as did Pall, Broughton, and Maass (21) in their measurements on ethylene. None of the above equations predict this rapid increase, an indication that the true value of  $(d^2P/dT^2)_\rho$  in this region must be much larger than that predicted by the above equations; there is a little precise PVT data available in this region to verify or refute this conclusion. The work of Pall *et al.* (21) suggests an alternate explanation, namely that the currently accepted model of phase behavior in this region may be too simple and that one-phase thermodynamic relations, for example Equations (1) and (2), may not apply.

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#### NOTATION

|            |                                                       |
|------------|-------------------------------------------------------|
| $C_p$      | = gross heat capacity of the calorimeter and contents |
| $C_p$      | = heat capacity at constant pressure                  |
| $C_p^*$    | = heat capacity at constant and zero pressure         |
| $C_v$      | = heat capacity at constant volume                    |
| $C_v^*$    | = heat capacity at constant volume and zero pressure  |
| $d$        | = differential operator                               |
| $f$        | = function                                            |
| $M$        | = mass                                                |
| $P$        | = absolute pressure                                   |
| $q$        | = power input                                         |
| $q_{mean}$ | = average power input                                 |
| $R$        | = universal gas constant                              |
| $T$        | = absolute temperature                                |
| $V$        | = specific volume                                     |
| $Z$        | = compressibility factor                              |
| $^*$       | = zero pressure or ideal gas state                    |
| $\Delta$   | = finite-change operator                              |
| $\theta$   | = time                                                |
| $\rho$     | = density                                             |

|                   |                                                         |
|-------------------|---------------------------------------------------------|
| $\Delta\theta$    | = time interval of power input                          |
| $\Delta T$        | = change in temperature                                 |
| $\Delta T_{corr}$ | = correction for the heat leakages from the calorimeter |

#### Constants

The following constants have been used throughout this research:

|                 |                                              |
|-----------------|----------------------------------------------|
| 1 cal.          | = 1 thermochemical cal. = 4.1840 absolute j. |
| Temperature °K. | = temperature °C. plus 273.16                |
| 1 atm.          | = 14.70 lb./sq. in.                          |

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