Measurement of the Isobaric Heat Capacity of Liquids and Certain Mixtures above the Normal Boiling Point

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Isobaric liquid head capacities were measured as a function of pressure at temperatures above the normal atmospheric boiling point in a closed-loop flow calorimeter. The liquids studied were benzene, toluene, *m*-xylene, cyclohexane, *n*-heptane, 1-butanol, a binary mixture of benzene and cyclohexane, and a ternary mixture of *n*-heptane, cyclohexane, and benzene. The results agreed to within 1% from data reported by other investigators in the temperature ranges where there was overlap. The temperature and pressure range covered was from 20 to 250 °C and from 5 to 40 bar. An extrapolation technique allowed one to obtain C_p values for the saturated liquid.

Few experimental data are available for liquid heat capacities at temperatures above the atmospheric boiling point. Yet the need for such data is urgent as the chemical process industry adopts processes where high temperatures and pressures are required.

In the present work, the isobaric liquid heat capacity was measured. It is defined as

$$C_p = (\partial H/\partial T)_p$$

It is not uncommon, however, to refer to a different liquid heat capacity, i.e., C_σ where

$$C_\sigma = (dH/dT)_{sat}$$

as experiments are carried out with a liquid–vapor system that is always maintained in phase equilibrium. These two properties are related.

$$C_p - C_\sigma = -(dP/dT)_{sat}[V_{sat} - T(\partial V/\partial T)_p]$$

At low temperatures, $C_p \sim C_\sigma$, but at temperatures much above the boiling point, C_p becomes significantly larger than C_σ.

Experimental Section

Liquid heat capacities were measured in a closed-loop flow calorimeter that could be operated between temperatures of 20 and 280 °C and pressures of 5–50 bar. The system is shown in schematic fashion in Figure 1. A high-pressure reciprocating pump (B) was fed from reservoir (A). The bladder accumulator (C) essentially eliminated pulsations and steady flow could be maintained up to 50 bars and 13 l./min. Pressure control was maintained by automatic valve (D) which by-passed liquid to the feed reservoir. Two hot-oil baths (E) containing Silicone oil were employed to heat the liquid to the test temperature. The outlet from these heaters could be controlled to within ±0.02 °C. After flowing through the calorimeter (F) which is described later, the liquid was cooled in a countercurrent water heat-exchanger (G) to about 25–30 °C. Next the stream temperature was reduced to 26.5 °C in a constant-temperature bath (H). The pressure was monitored with transducer I.

Flow control was varied with a regulating valve (J) which also reduced the pressure to near atmospheric. Flow measurement was made with a Cox turbine-flow meter (K). For each fluid used, the flow-meter was calibrated at the same temperature and pressure (26.5 °C and 1 bar) and these conditions were held constant and independent of the pressure and temperature in the calorimeter.

Filters, other valves, sampling probes, and additional instrumentation are not shown. A complete description of the system is available elsewhere (*16*).

The calorimeter is shown in Figure 2. The pressurized, preheated liquid enters through the insulated line at A′ and flows through a static mixer (I′). One set of 25-thermopile junctions and a thermocouple to monitor the inlet temperature were placed just prior to the heater (K′). The heater was a 38-cm long Teflon cross upon which was wrapped 14 m of 26-guage Nicrome heating wire; 90 W of electrical energy could be supplied with a maximum temperature difference between the wire and fluid of 2 K. Following the heater, before the second set of thermopile junctions, was a second static mixer to ensure uniformity of temperature. To reduce radiation losses, the outlet liquid was passed through a spiral coil wrapped around the inner calorimeter and exited via tube (B′). The outer vacuum vessel was insulated with aluminum foil radiation shields and Fiberglas mats and held below 1 mN/m^2 (10^{-5} Torr).

Normally the temperature rise of the fluid in the calorimeter was between 1.5 and 2 °C. The range of Reynolds numbers was 800–1200. All signal outputs were recorded with a Hewlett-Packard data acquisition system.

The turbine-flow meter was calibrated in situ for each substance. The maximum error in the mass flow rate measurement was estimated to be 0.35%. The estimated error in measuring the power input to the calorimeter heater was 0.03%. The temperature change across the calorimeter was measured with the 25-junction chromel–constantan thermopile with a precision ±0.003 °C, or ± 0.15% error for a 2 °C increase and 0.1% for heat losses determination. The system could be held in a steady state mode for periods longer than 30 min, but even here, small cyclic fluctuations were observed; therefore data were taken every 10 s, and the average of an integral number of oscillations was chosen as the time value. The estimated error contribution to the heat capacity measurement due to the fluctuations around the steady state is 0.5%. Summing all contributions, the maximum estimated error in the heat capacity measurement was 1%. The inlet and outlet temperatures were measured with copper–constantan thermocouples with a precision of ±0.2 °C and pressures were determined within ±0.1 bar. Accuracy in determining composition was estimated at 2%.

Results

Calculations. An energy balance for the steady-state calorimeter may be written as:

$$\dot{Q}_H - \dot{Q}_L = \dot{m}[C_p\Delta T + (\partial H/\partial P)_T\Delta P] \qquad (1)$$

ΔT is the measured temperature difference across the calorimeter corrected for small parasitic voltages that were determined as a function of temperature. $\dot{Q}_H$ is the power supplied to the calorimeter heater and $\dot{Q}_L$ represents the small power loss from heat transfer to the environment. The last term in eq 1 accounts for enthalpy changes due to the pressure drop in the calorimeter (about 0.03–0.04 bar). For each fluid and for each temperature level, duplicate runs were made with and without power to the heater. Designating ΔT_0 as the small measured temperature change, without power, from eq 1,

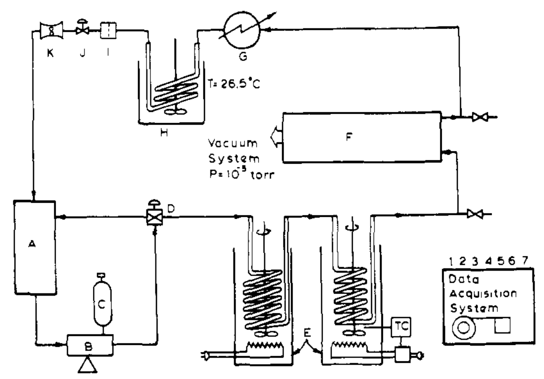
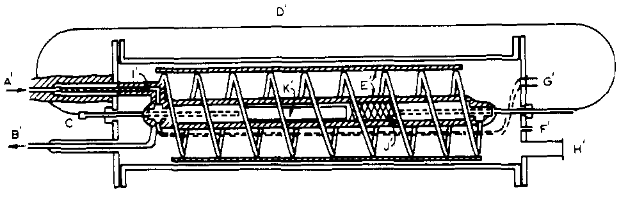


Figure 1. Flow schematic.



- A' Liquid Inlet
- B' Liquid Outlet
- C' Thermopile Connection
- D' Wires Connecting Thermopile Walls
- E' Radiation Shielding
- F' Connection for Vacuum Measurement
- G' Heater Power Terminals
- H' Vacuum Pump Connection
- I' Static Mixer
- J' Static Mixer
- K' Calorimeter Heater

Figure 2. Calorimeter.

$$\dot{m}C_p\Delta T_0 = -\dot{Q}_L - \dot{m}(\partial H/\partial P)_T\Delta P \equiv \phi(T) \qquad (2)$$

Neglecting terms of the order of $(d\phi/dT)\Delta T/2$ (less than 0.1 W compared to 70–90 W for $\dot{Q}_H$),

$$C_p = \dot{Q}_H/[\dot{m}(\Delta T - \Delta T_0)] \qquad (3)$$

eq 3 was used to calculate C_p with $\dot{Q}_H$, $\dot{m}$, ΔT, and ΔT_0 as measured variables.

Liquids Tested. Values of C_p were measured as a function of temperature and pressure for benzene, toluene, *m*-xylene, cyclohexane, a binary mixture of cyclohexane and benzene, and a ternary mixture of cyclohexane, benzene, and *n*-heptane. A few data points were also obtained for 1-butanol. Commercial chemicals specified as analytical reagents were used, and no further purification was attempted. Gas chromatography showed no impurities. The temperature range studied was from 20 to 250 °C; pressures always exceeded the vapor pressure.

In making test runs, for a given liquid, a pressure level was selected and C_p measured as a function of temperature. Each datum point was the average of test readings taken over a period of 10 min. By this means very small <0.05 °C cyclic variations in the inlet calorimeter inlet temperature were smoothed out. Typical test data for cyclohexane are shown in Figure 3. Excellent agreement is found with values of C_p reported by previous investigators (*3*) (*15*) at low temperatures except for those data noted by Parks et al. (*14*) which are 1–1.5% low. Auerbach et al. (*5*) report values of C_p up to 93 °C which are 2% low; these latter investigators did not measure C_p but, rather, the saturated liquid heat capacity and then they corrected for vapor pressure. No previous data were available at higher temperatures.

From the data shown in Figure 3, a C_p–P curve was constructed and isotherms plotted (Figure 4). The vapor pressure–temperature relation for cyclohexane delineated the saturation curve. From this figure C_p for cyclohexane may be determined from 125 to 250 °C (T_r = 0.72–0.95) and at pressures ranging from the vapor pressure to 40 bars. Note that on an isotherm the

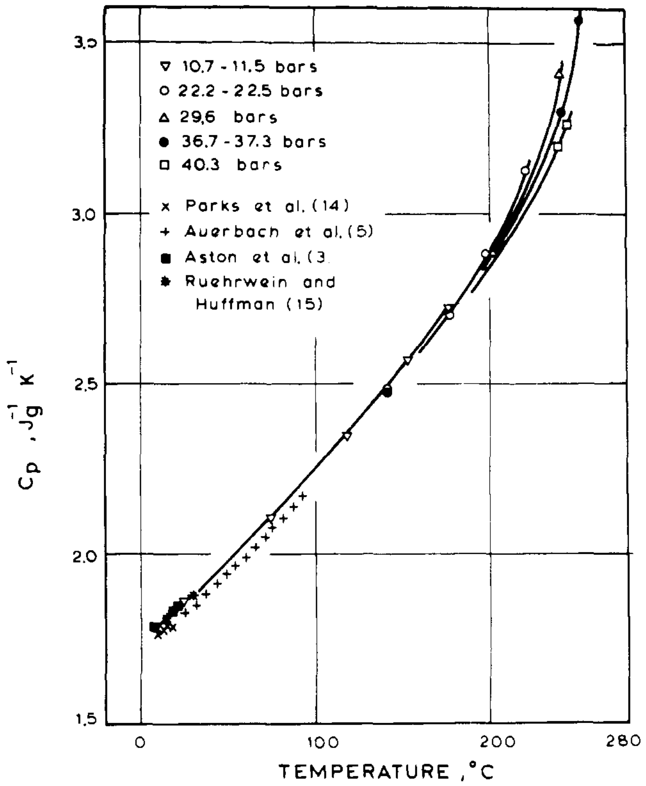


Figure 3. Experimental C_p for cyclohexane.

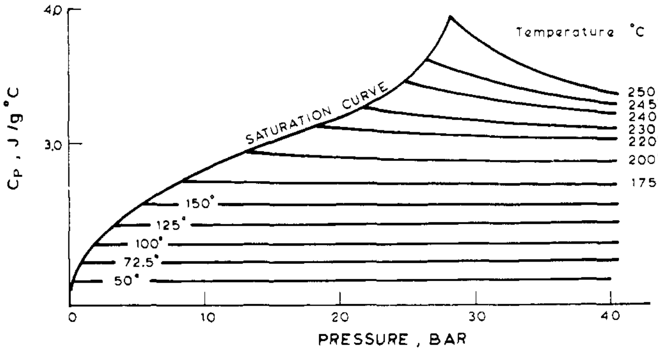


Figure 4. Cyclohexane, isobaric heat capacity.

effect of pressure on C_p is slight except at high reduced temperatures.

Experimental data were plotted on large graphs and smooth curves drawn through the data. Values of C_p were read at even temperature intervals and these are shown on Tables I–VII for all the compounds tested in this work. The uncertainty in the values shown is believed to be less than 1%.

n-Heptane Studies. Several investigators have reported heat capacity values for liquid *n*-heptane. On Figure 5, the C_p data from Amirkhanov et al. (*1*) are graphed and the data taken in this work are also shown. These data represent C_p values for the saturated liquid. Excellent agreement is obtained. Also shown in Figure 5 are data for C_σ up to 110 °C obtained by Douglas et al. (*8*) which is considered a liquid heat capacity standard below this temperature. Data from this latter work are not shown at higher temperatures because C_σ and C_p may differ significantly at high reduced temperatures.

Mixtures. Only two mixtures were studied but these included aliphatic, naphthenic, and aromatic hydrocarbons. The data obtained are of value to indicate the validity of the ideal-solution rule that is normally assumed for such mixtures, i.e., defining an *excess*-heat capacity, C_p^{Ex} as

Table I. Smoothed Cyclohexane Isobaric Liquid Heat Capacity, J g^{-1} K^{-1}

Temp, °C	C_p on sat curve	Pressure, bars 5	10	15	20	25	30	35	40
125	2.38	2.38	2.38	2.38	2.38	2.38	2.37	2.37	2.37
150	2.55		2.55	2.54	2.54	2.53	2.53	2.53	2.53
175	2.71		2.71	2.70	2.70	2.70	2.69	2.69	2.69
200	2.91			2.90	2.89	2.88	2.87	2.86	2.85
220	3.11				3.10	3.07	3.05	3.03	3.01
230	3.26					3.22	3.17	3.14	3.10
240	3.44					3.43	3.35	3.28	3.21
245	3.63						3.52	3.39	3.26
250	3.89						3.81	3.56	3.35

Table II. Smoothed Heat Capacity of Benzene, J g^{-1} K^{-1}

Temp, °C	C_p on sat curve	Pressure, bars 20	25	35
160	2.20	2.20	2.20	2.20
180	2.34	2.33	2.32	2.32
190	2.41	2.40	2.39	2.38
200	2.48	2.47	2.46	2.45
210	2.57	2.56	2.54	2.52
220	2.67		2.64	2.60

Table III. Smoothed Heat Capacity of Toluene, J g^{-1} K^{-1}

Temp, °C	C_p on sat curve	Pressure, bars 10	15	20	25
120	2.05	2.05	2.05	2.05	2.05
140	2.12	2.12	2.12	2.12	2.12
160	2.21	2.21	2.20	2.20	2.20
180	2.32	2.31	2.30	2.30	2.29
200	2.45	2.43	2.42	2.40	2.39
210	2.52	2.51	2.48	2.46	2.45
220	2.59		2.56	2.53	2.51
230	2.67		2.64	2.60	2.57

Table IV. *m*-Xylene, Isobaric Heat Capacity, J g^{-1} K^{-1}

Temp, °C	C_p on sat curve	Pressure, bars 10	15	20	25
138	2.13				
150	2.18				
170	2.26				
190	2.35				
210	2.44				
230	2.52				
250	2.62	2.62	2.60	2.59	2.59
267	2.78		2.73	2.69	2.67

Table V. Smoothed Liquid Heat Capacity of *n*-Heptane, J g^{-1} K^{-1}

Temp, °C	C_p on sat curve	Pressure, bars 10	15	20
140	2.70	2.70	2.69	2.69
160	2.81	2.80	2.79	2.79
180	2.94	2.93	2.91	2.90
200	3.08	3.08	3.06	3.05
210	3.18		3.16	3.13
220	3.32		3.31	3.26
230	3.55			3.46
240	3.85			3.77

Table VI. Smoothed Heat Capacity of a Mixture Benzene–Cyclohexane (Benzene Mole Fraction = 0.635), J g^{-1} K^{-1}

Temp, °C	Pressure, bars 15	20	30	40
180	2.46	2.46	2.45	2.44
190	2.54	2.53	2.51	2.50
200	2.61	2.60	2.58	2.56
210		2.69	2.66	2.64
220		2.80	2.76	2.74

Table VII. Smoothed Heat Capacity of a Mixture of Benzene–Cyclohexane–*n*-Heptane (Benzene Mole Fraction = 0.456, Cyclohexane = 0.263), J g^{-1} K^{-1}

Temp, °C	Pressure, bars 20	30	40
160	2.47	2.47	2.47
180	2.57	2.57	2.57
200	2.70	2.69	2.68
210	2.81	2.79	2.78
215	2.88	2.85	2.83
220	3.02	2.95	2.90

$$C_p^{Ex} = C_{p_{mix}} - \sum w_j C_{p_j} \tag{4}$$

If $C_p^{Ex} = 0$, the liquid mixture is ideal. In all cases C_p^{Ex} was found to be negative and of the order of 1–2% of $C_{p_{mix}}$. Atwood (*4*) measured the isobaric liquid heat capacity of benzene–cyclohexane mixtures from the freezing point to 30 °C. C_p^{Ex} was found to be about +0.005 J g^{-1}K^{-1} at a benzene mole fraction of 0.25; at a mole fraction of 0.75, $C_p^{Ex} \sim -0.0366$ J g^{-1}K^{-1}, a value in excellent agreement with the present work at 38 °C.

The general conclusion from these hydrocarbon mixture results is that, for reduced temperatures up to about 0.9, one may calculate the value of $C_{p_{mix}}$ from eq 4 assuming $C_p^{Ex} \sim 0$. For nonhydrocarbon systems, this simple rule cannot be assumed. For hydrocarbon mixtures, the critical temperature was estimated as a mole fraction average of the pure compound criticals.

1-Butanol. This alcohol was the only polar compound studied. Measurements were taken from 20 to 192 °C at a single pressure of 15 bar. The results are shown in Figure 6. In only one study (*17*) were data reported above 70 °C.

The most interesting aspect of Figure 6 is the inflection point at about 360 K (T_r = 0.65) with the curve becoming concave to the temperature axis above this value. When comparing with data for other alcohols (see Figure 7), inflection points are also noted for 2-propanol at T_r = 0.65 and at T_r = 0.6 for 2-butanol

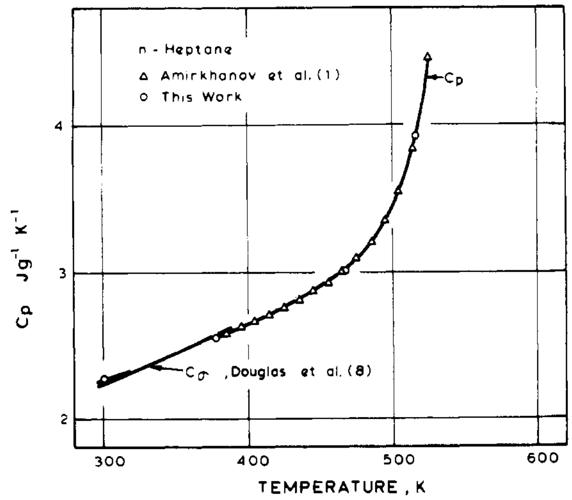


Figure 5. Experimental and reported values for *n*-heptane.

and 1-pentanol, but the 1-butanol data reported in this study, as well as by Stephens and Tamplin (*17*), show a significant curvature above $T_r = 0.7$.

At the present time no plausible reason is available to explain the unusual data for 1-butanol above a T_r value of 0.7. Chemical reaction (oxidation) in the calorimeter could be invoked but, since care was taken to exclude oxygen from the system and since only traces of esters or acids were found in the 1-butanol after testing, this hypothesis had to be rejected.

In summary, C_p for alcohols tends to be concave at a reduced temperature of 0.6–0.7. The data obtained for 1-butanol can be considered reliable up to a temperature of about 360 K. Further studies are needed to determine the behavior of these alcohols at higher temperatures.

Glossary

C_p	isobaric heat capacity (eq 1)
C_σ	saturated heat capacity (eq 2)
H	enthalpy
$\dot{m}$	mass flow rate through the calorimeter
Q	heat
P	pressure
T	temperature
V	volume
w	mass fraction

Subscripts

sat	along the saturation envelope

Literature Cited

(1) Amirkhanov, Kh. I., Alibekov, B. G., Vikhrov, D. I., Mirskaya, V. A., Levina, L. N., *High Temp. (Engl. Transl.)*, **9**, 1211 (1971).
(2) Andon, R. J. L., Connett, J. E., Counsell, J. F., Lees, E. B., Martin, J. F., *J. Chem. Soc. A*, 661 (1971).
(3) Aston, J. G., Szasz, G. J., Fink, H. L., *J. Am. Chem. Soc.*, **65**, 1135 (1943).
(4) Atwood, G. R., *Diss. Abstr.*, **18**, 1993 (1958).
(5) Auerbach, C. E., Sage, B. H., Lacey, W. N., *Ind. Eng. Chem.*, **42**, 110 (1950).
(6) Counsell, J. F., Hales, J. L., Martin, J. F., *Trans. Faraday Soc.*, **61**, 1869 (1965).
(7) Counsell, J. F., Lees, E. B., Martin, J. F., *J. Chem. Soc. A*, 1819 (1968).

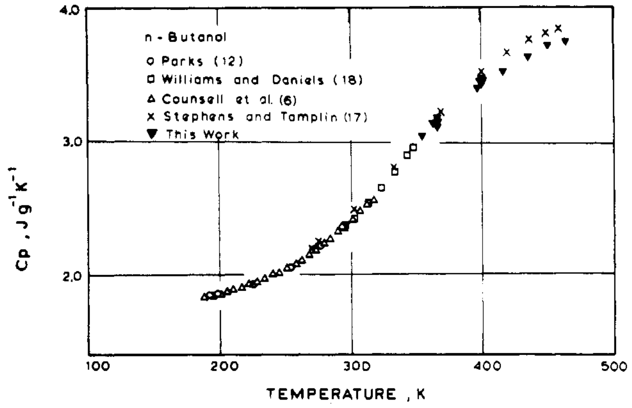


Figure 6. Experimental and reported C_p for 1-butanol.

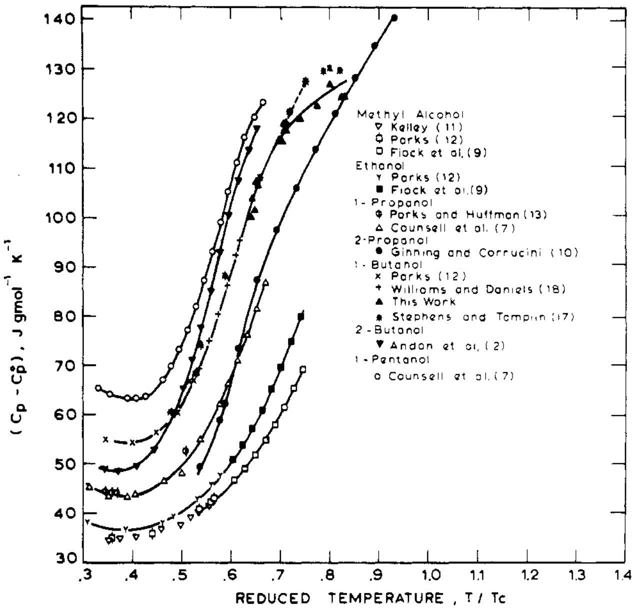


Figure 7. Heat capacity of alcohols vs. reduced temperature.

(8) Douglas, T. B., Furukawa, G. T., McCoskey, R. E., Ball, A. F., *J. Res. Natl. Bur. Stand.*, **53**, 139 (1954).
(9) Fiock, E. F., Ginnings, D. C., Holton, W. B., *J. Res. Natl. Bur. Stand.*, **6**, 881 (1931).
(10) Ginnings, D. C., Corruccini, R. J., *Ind. Eng. Chem.*, **40**, 1990 (1948).
(11) Kelley, K. K., *J. Am. Chem. Soc.*, **51**, 180 (1929).
(12) Parks, G. S., *J. Am. Chem. Soc.*, **47**, 338 (1925).
(13) Parks, G. S., Huffman, H. M., *J. Am. Chem. Soc.*, **48**, 2788 (1926).
(14) Parks, G. S., Huffman, H. M., Thomas, S. B., *J. Am. Chem. Soc.*, **52**, 1032 (1930).
(15) Ruehrwein, R. A., Huffman, H. M., *J. Am. Chem. Soc.*, **65**, 1620 (1943).
(16) San José, J. L., Sc.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1975.
(17) Stephens, M., Tamplin, W. S., personal communication, Union Carbide Corp., So. Charleston, W.Va., 1976.
(18) Williams, J. W., Daniels, F., *J. Am. Chem. Soc.*, **46**, 903 (1924).

Received for review December 15, 1975. Accepted June 4, 1976. Acknowledgment is made to the National Science Foundation and also to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. J. L. San José was partially supported by the Consejo Nacional de Ciencia y Tecnologia of Mexico.