# Densities of Some Organic Substances

**Suresh Nayar and Arvind P. Kudchadker[1]**
*Department of Chemical Engineering, Indian Institute of Technology, Kanpur 208016, India*

The densities in air of cycloheptane, n-nonanol, 2-methylcyclohexanol, benzaldehyde, chlorobenzene, and bromobenzene were measured from about 25° to 100°C with a modified Robertson pycnometer. Triple-distilled mercury was used for calibrating the pycnometers at each temperature of investigation. The accuracy of the density measurements was estimated to be ±0.0005 g cm$^{-3}$ or better. The experimental data for each compound were fitted to nth degree polynomials in temperature for interpolation and limited extrapolation. The agreement with the literature values is satisfactory.

As part of the program for the experimental determinations of certain physical and thermodynamic properties of organic substances, density measurements in air are reported for cycloheptane, n-nonanol, 2-methylcyclohexanol, benzaldehyde, chlorobenzene, and bromobenzene from 27.30° to 96.55°C at approximately 10° intervals. The experimental details have been reported by Abraham et al. (1).

## Materials

Cycloheptane, chlorobenzene, and bromobenzene were analar-grade samples obtained from Fluka A.G., Buchs, Switzerland, and were used without further purification. Analar-grade n-nonanol was supplied by Aldrich Chemicals, Milwaukee, Wis., USA, and was used as such. Benzaldehyde was laboratory-grade sample obtained from Aniline Dyestuffs Ltd., Bombay, India, and

[1] To whom correspondence should be addressed.

was purified by fractional distillation under vacuum in a 20-plate sieve column of 2.54-cm i.d. at a 5:1 reflux ratio. Laboratory-grade methylcyclohexanol was supplied by Riedel Co., Germany. It was purified by successive fractional distillations in the above column, and the purity after each distillation was checked on a differential ebulliometer (4).

An essential difficulty in purifying methylcyclohexanol is its formation of 12 isomers (arising out of the combination of ortho, meta, and para positions with cis and trans conformations and dextro and levo rotatory behaviors). These isomers are spread over a large boiling range. The boiling range reported by the Riedel Co. was 165–173°C. The normal boiling point (at 760-mm Hg pressure) for the sample used in the present investigation was 168.42°C as determined in the differential ebulliometer. The density and refractive index were $d_4^{19.7} = 0.9231$ g cm$^{-3}$ and $n^{19.7}D = 1.4609$. On comparison with the literature (10), the sample was 2-methylcyclohexanol [literature value (10): boiling point at 760 mm Hg = $167.2 - 167.6°C$; $d_4^{19.7} = 0.9241$ g cm$^{-3}$; $n^{19.7}D = 1.4613$].

## Results

The experimental data are reported in Table I. Calibration of the pycnometers was carried out by using triple-distilled mercury. The density–temperature data for mercury were obtained from ref. 10. Each observation was duplicated satisfactorily by the use of two pycnometers. All corrections to the measured data were made as described earlier (1). The data for each compound were fitted to the second, third, or fourth-degree polynomials in temperature, and the constants of the "best" fit are given

**Table I. Experimental Values of Density in g cm$^{-3}$ Vs. Temperature for Compounds Investigated**

| t, °C | Cycloheptane | n-Nonanol | 2-Methylcyclo-hexanol | Benzaldehyde | Chlorobenzene | Bromobenzene |
|---|---|---|---|---|---|---|
| 27.30 | 0.80480 | 0.82339 | 0.91776 | 1.0397 | 1.0984 | 1.4854 |
| 37.12 | 0.79662 | 0.81677 | 0.90937 | 1.0304 | 1.0876 | 1.4722 |
| 47.74 | 0.78763 | 0.80911 | 0.90127 | 1.0205 | 1.0765 | 1.4578 |
| 57.68 | 0.77910 | 0.80240 | 0.89304 | 1.0114 | 1.0657 | 1.4448 |
| 67.66 | 0.77041 | 0.79457 | 0.88477 | 1.0024 | 1.0549 | 1.4315 |
| 76.87 | 0.76228 | 0.78806 | 0.87619 | 0.99424 | 1.0439 | 1.4181 |
| 86.63 | 0.75354 | 0.78030 | 0.86683 | 0.98568 | 1.0326 | 1.4035 |
| 96.55 | 0.74455 | 0.77224 | 0.85781 | 0.97711 | 1.0209 | 1.3894 |

**Table II. Regression Constants of Following Density Model for Compounds Investigated**

$d = A_0 + A_1T + A_2T^2 + A_3T^3$

d, g cm$^{-3}$; T, K

| Compound | $A_0$ | $A_1 \times 10^{-3}$ | $A_2 \times 10^{-6}$ | $A_3 \times 10^{-7}$ | Abs av dev | Max dev |
|---|---|---|---|---|---|---|
| Cycloheptane | 0.997387 | −0.454838 | −0.619601 | ... | ±0.0001 | +0.0003 |
| n-Nonanol | 0.927999 | −0.0325735 | −1.05093 | ... | ±0.0001 | +0.0003 |
| 2-Methylcyclohexanol | 1.01049 | +0.139793 | −1.49594 | ... | ±0.0002 | +0.0005 |
| Benzaldehyde | 1.38467 | −1.34763 | +0.663290 | ... | ±0.0002 | +0.0003 |
| Chlorobenzene | 2.27891 | −9.11762 | +25.1359 | −0.261827 | ±0.0002 | +0.0004 |
| Bromobenzene | 1.74269 | −0.430199 | −1.42156 | ... | ±0.0003 | −0.0006 |

**Table III. Comparison of Our Results with Literature Values**

| Compound | Lit values[a] | Our values[a] |
|---|---|---|
| Cycloheptane | $0.8109^{20}$ (10) | $0.8108^{20}$ |
| n-Nonanol | $0.8273^{20}$ (10); $0.8280^{20}$, $0.8247^{25}$, $0.8215^{30}$ (8) | $0.8281^{20}$, $0.8249^{25}$, $0.8215^{30}$ |
| 2-Methylcyclohexanol | $0.9194^{26}$ (10) | $0.9184^{26}$ |
| Benzaldehyde | $1.0415^{25}$ (10) | $1.0418^{25}$ |
| Chlorobenzene | $1.1065^{20}$, $1.1013^{25}$ (6); $1.10112^{25}$ (2) | $1.1065_8^{20}$, $1.1009_8^{25}$, $1.0954_6^{30}$ |
| | $1.10654^{20}$, $1.10118^{25}$, $1.09574^{30}$, $1.08484^{40}$ (7) | $1.0900_0^{35}$, $1.08460^{40}$, $1.0761^{47.9}$ |
| | $1.0901^{35}$, $1.0690^{55}$, $1.0415^{80.4}$, $1.0235^{96.1}$ (5) | $1.0685^{55}$, $1.0561^{66.4}$, $1.0464^{75.1}$ |
| | $1.0955^{30.1}$, $1.0763^{47.9}$, $1.0562^{66.4}$, $1.0470^{75.1}$ $1.0251^{94.8}$ (9) | $1.0408^{80.4}$, $1.0228^{94.8}$, $1.0212^{96.1}$ |
| Bromobenzene | $1.49500^{20}$, $1.48824^{25}$, $1.48150^{30}$ (3) | $1.4944^{20}$, $1.4880_5^{25}$, $1.4816_3^{30}$ |
| | $1.4841^{28.3}$, $1.4553^{49.5}$, $1.4392^{61.4}$, $1.4257^{71.2}$ (5) | $1.4838^{28.3}$, $1.4559^{49.5}$ $1.4397^{61.4}$, $1.4260^{71.2}$ |

[a] Superscript denotes temperature, °C.

in Table II along with the average and maximum deviations. The regression analysis was carried out with an IBM 7044 computer. The accuracy in the experimental values was estimated to be within $\pm 0.0005$ g cm$^{-3}$ (1).

## Discussion

Comparison of our results with the literature values is reported in Table III. The agreement for cycloheptane, methylcyclohexanol, and benzaldehyde with the limited literature values is satisfactory. For n-nonanol our values agree very well with the Thermodynamics Research Center selected values (8). For chlorobenzene the agreement with the measurements of Nyvlt and Erdos (7) from 20° to 40°C is within our assigned uncertainty. However, at higher temperatures our values are lower than those reported by Meyer and Mylius in 1920 (5) and Velasco in 1927 (9). For bromobenzene our values agree very well with those of Dreisbach and Martin (3) and Meyer and Mylius (5).

## Literature Cited

(1) Abraham, T., Bery, V., Kudchadker, A. P., J. Chem. Eng. Data, **16**, 355 (1971).
(2) Brown, I., Aust. J. Sci. Res., **A5**, 530 (1952).
(3) Dreisbach, R. R., Martin, R. A., Ind. Eng. Chem., **41**, 2875 (1949).
(4) Khanna, A., M. tech. thesis, Indian Institute of Technology, Kanpur 208016, U.P., India, February 1972.
(5) Meyer, J., Mylius, B., Z. Phys. Chem., **95**, 355 (1920).
(6) Mumford, S. A., Phillips, J. W. C., J. Chem. Soc., **1950**, p 75.
(7) Nyvlt, J., Erdos, E., Collect. Czech. Chem. Commun., **26**, 500 (1961).
(8) "Selected Values of Properties of Chemical Compounds," Thermodynamics Research Center Data Project, Thermodynamics Research Center, Texas A&M University, College Station, Tex. (looseleaf data sheets, extant 1972).
(9) Velasco, M., An. Soc. Espan. Fis. Quim., **25**, 252 (1927).
(10) Weast, R. C., "Handbook of Chemistry and Physics," 51st ed., Chemical Rubber Publ., Cleveland, Ohio, 1970.

# Enthalpy of Formation of Triammonium Hydrogen Pyrophosphate Monohydrate, (NH4)3HP2O7·H2O

**Basil B. Luff,[1] Robert B. Reed, and Zachary T. Wakefield**
*Division of Chemical Development, Tennessee Valley Authority, Muscle Shoals, Ala. 35660*

The enthalpy of formation from the elements in their standard states at 25°C of crystalline (triclinic) triammonium hydrogen pyrophosphate monohydrate, $(NH_4)_3HP_2O_7 \cdot H_2O$, is $-712.7$ kcal mol$^{-1}$. It was determined from the enthalpies of solution of $(NH_4)_3HP_2O_7 \cdot H_2O$, $H_3PO_4 \cdot 16.24H_2O$, $NH_4H_2PO_4$, and $H_2O$ in $10m$ HCl at 40°C and from published values for the heat capacities of these compounds and enthalpies of formation of $H_3PO_4$ and $NH_4H_2PO_4$.

A continuing study of the thermal properties of compounds of interest in fertilizer technology included a determination of the enthalpy of formation at 25°C of triammonium hydrogen pyrophosphate monohydrate, $(NH_4)_3HP_2O_7 \cdot H_2O$, a major component of ammonium polyphosphate fertilizers.

[1] To whom correspondence should be addressed.

## Materials and Apparatus

*Salts and acids.* Samples of $(NH_4)_3HP_2O_7 \cdot H_2O$ (GFW = 247.0824) were taken from the charge in a low-temperature calorimeter after the heat capacity had been measured (9). The pyrophosphate was prepared originally from a granular ammonium polyphosphate produced in a TVA pilot plant. A saturated solution of the polyphosphate had a pH of about 4.6, and 83% of the phosphorus was present as pyrophosphate. In the first step of purification, $(NH_4)_3HP_2O_7 \cdot H_2O$ about 93% pure was obtained by simultaneously adding concentrated NH4OH and solid ammonium polyphosphate to the saturated solution of the ammonium polyphosphate in the proportions to maintain the pH at 5.5. The crystalline product was filtered off and redissolved to saturation in distilled water at 25°C, and the solution was stored at 0°C to effect slow crystallization. The low-temperature recrystallization was repeated three times. The largest single crystals (several centimeters long) were removed, blotted free of mother liquor with absorbent paper, and stored in a sealed glass bottle.