Densities of Hydrochloric, Hydrobromic, Hydriodic, and Perchloric Acids from 25 to 75 °C at 1 atm

Thelma M. Herrington,* Alan D. Pethybridge, and Michael G. Roffey

Department of Chemistry, University of Reading, Whiteknights, Reading RG6 2AD, England

A weight dilatometer has been used to measure the densities of aqueous solutions of hydrochloric, hydrobromic, hydriodic, and perchloric acids up to 3 *m* at 10 °C intervals in the range 25-75 °C at 1.013 bar. The precision of the densities is ±1 × 10^{-5} g cm^{-3}. The data are compared with literature values where available.

Introduction

Solution densities at high temperatures are needed for many laboratory studies of water circuit problems, e.g., corrosion in boiler water and cooling systems. In order to obtain density data at high temperatures it is necessary to have a good knowledge of the density at lower temperatures. Currently there is a great lack of solution density data at temperatures other than room temperature. Although a great many compounds have been studied at 25 °C, very few of these have been extended even up to 100 °C. In this work we have been interested in developing a technique which may then be relatively easily adapted to measuring densities under pressure at high temperatures. The technique may then be used to provide the basic low-temperature data needed in the high-temperature study.

Experimental Section

Materials. Aristar grades of hydrochloric, hydrobromic, and perchloric acids were used without further purification. Hydriodic acid was purified before use. Analar-grade hydriodic acid was taken and any dissolved oxygen removed by passing oxygen-free nitrogen through the solution. Any free iodine present in the solution due to oxidization was then removed by successive extractions with BDH Amberlite LA-2 resin in carbon tetrachloride (*1*). The resultant clear solutions were then degassed, stored under nitrogen, and then used as quickly as possible after purification to eliminate the possibility of further oxidization. All the operations during this purification process were carried out under nitrogen in a glovebox. Carbonate-free solutions of sodium hydroxide were prepared by precipitation of sodium carbonate using the method described by Vögel (*2*). The carbonate-free solutions were then stored under nitrogen in blacked-out containers until use.

The acid solutions were degassed by boiling under reduced pressure for 0.5 h before standardization. Solutions of 0.1 M NaOH were made up from carbonate-free stock solutions. These solutions were then standardized by titration against weighed portions of a potassium hydrogen phthalate solution, which had been made up by weight, using a Metrohm 636 Titroprocessor in conjunction with a Metrohm E635 Dosimat unit. This procedure gave a reproducibility of better than 0.005% between titrations. A suitable weight dilution of the stock acid was then titrated against the standard alkali in the same manner.

All solutions were prepared by using demineralized water which was first distilled and then passed through a high-purity-grade, mixed-bed ion-exchange resin, followed by a filter column until its conductivity was less than 0.05 μS cm^{-1}. All mercury used was recovered and cleaned by a four-stage process, dried by passing air through it in contact with Analar-grade acetone, and stored under nitrogen in plastic containers until use.

Solutions were made up by weight, and buoyancy corrections applied. The air density at the time of weighing was calculated from tables (*3*). Two balances were used during this work: firstly a Stanton SM12 double-pan balance, used in conjunction with a set of NPL calibrated stainless steel weights, and secondly a Sartorius 2004 MP electronic balance. Both balances gave a precision of ±2 × 10^{-5} g and operated over a range of 0-160 g. The two balances agreed to within ±1 × 10^{-5} g on a given weight.

Dilatometer. The method chosen for this work was that of the weight dilatometer of Gibson and Loeffler (*4*). The principle of operation is that mercury is displaced through a capillary from a sealed vessel and collected in a preweighed pot. The advantage of this method is that it allows a large number of measurements to be made over several temperatures, giving a precision of ±1 × 10^{-5} g cm^{-3}, without refilling the dilatometer. The dilatometer was sealed by a brass clamp over the glass flange with a silicone rubber seating. Values for the density of water were taken from the compilation of Kell (*5*) and for the density of mercury from ref 3. The temperature of the water thermostat was monitored with a National Physical Laboratory calibrated platinum resistance thermometer, in conjunction with an Automatic Systems Laboratories precision ac double transformer ratio bridge (Model H6), to ±1 × 10^{-3} K. Temperature control was better than ±2 × 10^{-3} K.

Results and Discussion

The results of density measurements for hydrochloric, hydrobromic, hydriodic, and perchloric acids are given in Tables I-IV. The concentration range covered was up to 3.0 *m*. Few measurements were carried out below 0.5 *m*, as a precision of ±1 × 10^{-5} g cm^{-3} in the density gives an error of ±0.02 cm^3 mol^{-1} in the apparent molar volume at 0.5 *m* but ±0.1 cm^3 mol^{-1} at 0.1 *m*. From the density data the apparent molar volume of each solution was calculated from eq 1. The

$$^{\phi}V = (1/m)\{1/\rho - 1/\rho_0\} + M_2/\rho \qquad (1)$$

apparent molar volume data were smoothed by fitting to an extended form of the Debye-Hückel equation derived by Pitzer (*6*)

$$^{\phi}V - [^{\phi}V^{st} - {}^{\phi}V^{\infty}] = {}^{\phi}V^{\infty} + 2RTm(\partial\beta^0/\partial P)_T + (4RTm/\alpha^2)(\partial\beta^1/\partial P)_T[1 - (1 + \alpha m^{1/2})e^{-\alpha m^{1/2}}] + RTm^2(\partial C^{\phi}/\partial P)_T$$

where

$$^{\phi}V^{st} - {}^{\phi}V^{\infty} = (A_v/b)\ln(1 + bm^{1/2}) \qquad (2)$$

$b = 1.2$ $kg^{1/2}$ $mol^{-1/2}$ and $\alpha = 2.0$ $kg^{1/2}$ $mol^{-1/2}$. A_v is the Debye-Hückel slope, with the values taken from Bradley and Pitzer (*7*). The values of the apparent molar volume at infinite dilution and the fitting parameters were obtained by nonlinear regression. These values together with the standard deviations are given in Tables V-VIII.

By using the fitting parameters, one can calculate values of $^{\phi}V$ (smoothed) at very low concentration. The relative apparent molar volume $^{\phi}V^{rel}$ ($^{\phi}V^{rel} = {}^{\phi}V$(smoothed) − $^{\phi}V^{\infty}$) is plotted against $m^{1/2}$) at 25 °C for the halogen acids in Figure 1. The

0021-9568/85/1730-0264$01.50/0

Table I. Density of Hydrochloric Acid

$m/(\mathrm{mol\ kg^{-1}})$	$\rho/(\mathrm{g\ cm^{-3}})$ 298.15 K	308.15 K	318.15 K	328.15 K	338.15 K	348.15 K
1.2031	1.017 54	1.014 26	1.010 35	1.005 90	1.000 94	0.995 51
1.4839	1.022 02	1.018 69	1.014 74	1.010 28	1.005 34	0.999 96
1.6184	1.024 14	1.020 78	1.016 81	1.012 35	1.007 42	1.002 07
1.8511	1.027 77	1.024 37	1.020 35	1.015 89	1.010 97	1.005 66
2.0958	1.031 53	1.028 09	1.024 04	1.019 57	1.014 66	1.009 39
2.1148	1.031 83	1.028 38	1.024 33	1.019 85	1.014 95	1.009 68
2.1950	1.033 05	1.029 59	1.025 53	1.021 05	1.016 15	1.010 90
2.2648	1.034 11	1.030 64	1.026 57	1.022 09	1.017 19	1.011 95
2.3955	1.036 10	1.032 61	1.028 52	1.024 03	1.019 14	1.013 92
2.4579	1.037 04	1.033 55	1.029 45	1.024 96	1.020 07	1.014 86
2.7641	1.041 66	1.038 13	1.034 00	1.029 50	1.024 63	1.019 47
2.9574	1.044 57	1.041 03	1.036 88	1.032 37	1.027 52	1.022 38

Table II. Density of Hydrobromic Acid

$m/(\mathrm{mol\ kg^{-1}})$	$\rho/(\mathrm{g\ cm^{-3}})$ 298.15 K	308.15 K	318.15 K	328.15 K	338.15 K	348.15 K
0.5805	1.028 69	1.025 41	1.021 40	1.016 77	1.011 54	1.005 80
0.8286	1.041 94	1.038 54	1.034 45	1.029 76	1.024 49	1.018 74
1.0027	1.051 14	1.047 66	1.043 50	1.038 77	1.033 49	1.027 72
1.0813	1.055 26	1.051 74	1.047 56	1.042 82	1.037 52	1.031 75
1.1011	1.056 30	1.052 77	1.048 58	1.043 83	1.038 53	1.032 76
1.3334	1.068 38	1.064 74	1.060 47	1.055 67	1.050 33	1.044 54
1.5080	1.077 36	1.073 64	1.069 31	1.064 46	1.059 10	1.053 30
1.5271	1.078 34	1.074 60	1.070 27	1.065 42	1.060 05	1.054 25
1.6768	1.085 97	1.082 16	1.077 78	1.072 89	1.067 49	1.061 68
1.9560	1.100 03	1.096 09	1.091 61	1.086 64	1.081 21	1.075 37
1.9566	1.100 06	1.096 12	1.091 64	1.086 67	1.081 24	1.075 40
2.3224	1.118 17	1.114 05	1.109 44	1.104 37	1.098 87	1.093 00
2.9698	1.149 31	1.144 89	1.140 04	1.134 78	1.129 16	1.123 22

Table III. Density of Hydriodic Acid

$m/(\mathrm{mol\ kg^{-1}})$	$\rho/(\mathrm{g\ cm^{-3}})$ 298.15 K	308.15 K	318.15 K	328.15 K	338.15 K	348.15 K
0.2116	1.016 24	1.013 07	1.009 04	1.004 48	0.999 29	0.993 58
0.3662	1.030 18	1.026 90	1.022 71	1.018 13	1.012 90	1.007 19
0.5679	1.048 28	1.044 85	1.040 45	1.035 84	1.030 56	1.024 83
0.6773	1.058 06	1.054 54	1.050 03	1.045 39	1.040 08	1.034 36
0.8142	1.070 23	1.066 62	1.061 96	1.057 31	1.051 97	1.046 24
0.9341	1.080 87	1.077 15	1.072 37	1.067 70	1.062 33	1.056 59
1.1262	1.097 81	1.093 95	1.088 96	1.084 27	1.078 85	1.073 11
1.3859	1.120 56	1.116 50	1.111 23	1.106 50	1.101 03	1.095 25
1.5793	1.137 37	1.133 17	1.127 70	1.122 93	1.117 42	1.111 62
1.6622	1.144 54	1.140 29	1.134 72	1.129 93	1.124 41	1.118 60
1.8432	1.160 15	1.155 75	1.149 99	1.145 18	1.139 62	1.133 78
2.1303	1.184 70	1.180 10	1.174 01	1.169 16	1.163 54	1.157 66
2.4860	1.214 81	1.209 93	1.203 45	1.198 54	1.192 86	1.186 91

Table IV Density of Perchloric Acid

$m/(\mathrm{mol\ kg^{-1}})$	$\rho/(\mathrm{g\ cm^{-3}})$ 298.15 K	308.15 K	318.15 K	328.15 K	338.15 K	348.15 K
0.2427	1.010 46	1.007 11	1.003 05	0.998 30	0.992 97	0.987 00
0.4719	1.022 86	1.019 20	1.014 90	1.009 94	1.004 44	0.998 28
0.7070	1.035 32	1.031 37	1.026 83	1.021 66	1.015 99	1.009 67
0.9560	1.048 26	1.044 02	1.039 21	1.033 84	1.027 99	1.021 55
1.1962	1.060 50	1.055 99	1.050 94	1.045 37	1.039 36	1.032 84
1.4622	1.073 78	1.068 99	1.063 67	1.057 90	1.051 70	1.045 12
1.7193	1.086 37	1.081 31	1.075 75	1.069 79	1.063 41	1.056 78
1.9887	1.099 30	1.093 99	1.088 18	1.082 01	1.075 47	1.068 77
2.2979	1.113 85	1.108 24	1.102 17	1.095 78	1.089 04	1.082 25
2.5407	1.125 05	1.119 23	1.112 96	1.106 40	1.099 51	1.092 62
2.8181	1.137 65	1.131 57	1.125 11	1.118 34	1.111 30	1.104 23
3.1306	1.151 59	1.145 22	1.138 58	1.131 56	1.124 37	1.117 02

Table V Fitting Parameters for Hydrochloric Acid

T/K	${}^{\phi}V^{\infty}/(\mathrm{cm^3\ mol^{-1}})$	$10^5(\partial\beta^0/\partial P)/$ $(\mathrm{kg\ mol^{-1}\ atm^{-1}})$	$10^5(\partial\beta^1/\partial P)/$ $(\mathrm{kg^2\ mol^{-2}\ atm^{-1}})$	$10^6(\partial C^{\phi}/\partial P)/$ $(\mathrm{kg^2\ mol^{-2}\ atm^{-1}})$	SD of fit
298.15	17.803 ± 0.084	−1.068 ± 0.462	3.625 ± 1.067	−3.627 ± 0.368	0.002
308.15	18.131 ± 0.071	−2.131 ± 0.378	5.908 ± 0.871	−4.470 ± 0.301	0.001
318.15	18.022 ± 0.068	−1.936 ± 0.352	5.721 ± 0.813	−4.966 ± 0.281	0.001
328.15	17.751 ± 0.044	−1.636 ± 0.222	5.109 ± 0.512	−4.881 ± 0.177	0.001
338.15	17.459 ± 0.060	−1.901 ± 0.291	5.859 ± 0.671	−5.412 ± 0.232	0.001
348.15	17.013 ± 0.093	−1.745 ± 0.437	5.340 ± 1.008	−5.011 ± 0.348	0.002

Table VI. Fitting Parameters for Hydrobromic Acid

T/K	$^{\phi}V^{\infty}$/(cm^3 mol^{-1})	$10^5(\partial\beta^0/\partial P)$/ (kg mol^{-1} atm^{-1})	$10^5(\partial\beta^1/\partial P)$/ (kg^2 mol^{-2} atm^{-1})	$10^6(\partial C^{\phi}/\partial P)$/ (kg^2 mol^{-2} atm^{-1})	SD of fit
298.15	25.074 ± 0.015	−3.289 ± 0.102	5.339 ± 0.268	1.322 ± 0.162	0.002
308.15	25.373 ± 0.018	−3.354 ± 0.124	5.425 ± 0.325	1.249 ± 0.197	0.003
318.15	25.510 ± 0.016	−3.298 ± 0.106	5.104 ± 0.277	1.643 ± 0.168	0.002
328.15	25.492 ± 0.018	−3.400 ± 0.115	5.319 ± 0.300	1.648 ± 0.182	0.002
338.15	25.468 ± 0.024	−3.912 ± 0.145	6.352 ± 0.378	1.515 ± 0.229	0.003
348.15	25.280 ± 0.012	−4.231 ± 0.069	6.971 ± 0.182	1.476 ± 0.110	0.002

Table VII. Fitting Parameters for Hydriodic Acid

T/K	$^{\phi}V^{\infty}$/(cm^3 mol^{-1})	$10^5(\partial\beta^0/\partial P)$/ (kg mol^{-1} atm^{-1})	$10^5(\partial\beta^1/\partial P)$/ (kg^2 mol^{-2} atm^{-1})	$10^6(\partial C^{\phi}/\partial P)$/ (kg^2 mol^{-2} atm^{-1})	SD of fit
298.15	36.372 ± 0.013	−7.792 ± 0.132	7.250 ± 0.425	5.280 ± 0.476	0.006
308.15	36.893 ± 0.008	−7.863 ± 0.077	7.605 ± 0.250	4.770 ± 0.280	0.003
318.15	37.654 ± 0.009	−7.877 ± 0.084	7.688 ± 0.270	4.797 ± 0.302	0.004
328.15	37.591 ± 0.015	−8.407 ± 0.135	9.172 ± 0.437	3.967 ± 0.488	0.006
338.15	37.476 ± 0.016	−8.326 ± 0.145	8.898 ± 0.468	4.296 ± 0.523	0.007
348.15	37.109 ± 0.020	−8.552 ± 0.171	9.698 ± 0.551	4.016 ± 0.617	0.009

Table VIII. Fitting Parameters for Perchloric Acid

T/K	$^{\phi}V^{\infty}$/(cm^3 mol^{-1})	$10^5(\partial\beta^0/\partial P)$/ (kg mol^{-1} atm^{-1})	$10^5(\partial\beta^1/\partial P)$/ (kg^2 mol^{-2} atm^{-1})	$10^6(\partial C^{\phi}/\partial P)$/ (kg^2 mol^{-2} atm^{-1})	SD of fit
298.15	44.097 ± 0.009	−2.855 ± 0.082	4.689 ± 0.236	−1.571 ± 0.187	0.004
308.15	45.445 ± 0.005	−3.227 ± 0.043	4.456 ± 0.123	−0.229 ± 0.098	0.002
318.15	46.356 ± 0.008	−3.133 ± 0.068	4.340 ± 0.194	−1.017 ± 0.154	0.003
328.15	47.268 ± 0.005	−3.485 ± 0.039	4.479 ± 0.113	−0.106 ± 0.090	0.002
338.15	48.024 ± 0.006	−4.160 ± 0.050	5.920 ± 0.143	−0.736 ± 0.113	0.003
348.15	49.194 ± 0.011	−5.380 ± 0.080	5.876 ± 0.230	4.266 ± 0.182	0.004

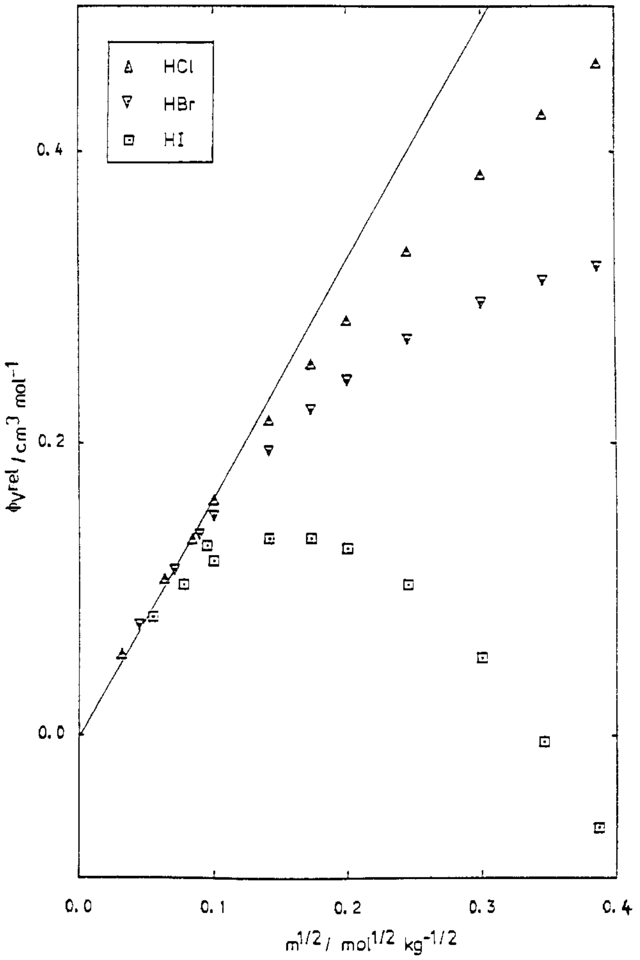

Figure 1. Comparison of values of $^{\phi}V^{rel}$ for the halogen acids at 25 °C.

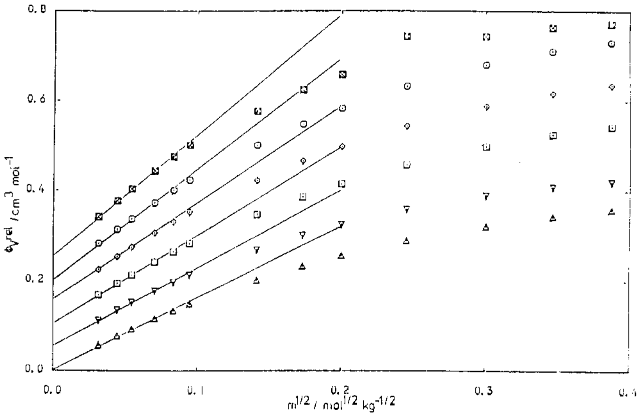

Figure 2. Values of $^{\phi}V^{rel}$ for perchloric acid: (△) 25, (▽) 35, (□) 45, (◇) 55, (○) 65, (□) 75 °C.

Table IX. Values of $^{\phi}V^{\infty}$ for HCl 25 °C

no.	($^{\phi}V^{\infty}$/ (cm^3 mol^{-1})	method of measurement	concn. range (mol kg^{-1})	ref
1	17.80	weight dilatometer	0.5–3.0	this work
2	17.76	calcd from results of Redlich (9)		10
3	17.80	mercury displacement	0.2–2.0	11
4	17.82	dilatometer	0.001–1.0	12
5	18.0	calcd from ICT (*13*)		14
6	18.07	sinker	0.04–4.0	15
7	18.20	calcd from results of Geffken (*16*)		17

slope approaches A_v/b as $m^{1/2}$ tends to zero (*8*). It can be seen that the deviation from linearity increases for the acids in the order HCl < HBr < HI. In Figure 2 $^{\phi}V^{rel}$ is plotted against $m^{1/2}$ for perchloric acid; the curves for successive 10 °C temperature increases are offset by a constant increment of 0.05 cm^3 mol^{-1} for reasons of clarity. A negative deviation from the limiting slope A_v/b is shown at all temperatures.

The values for the apparent molar volume at infinite dilution, $^{\phi}V^{\infty}$, at 25 °C were compared where possible with existing literature data. Where sufficient data are available, the quoted results have been fitted to eq 2.

Hydrochloric Acid. A great many values of $^{\phi}V^{\infty}$ for HCl have been reported lying in a range from 17.76 to 18.20 cm^3

mol^{-1}. These values are shown in Table IX. The currently accepted value for $^{\phi}V^{\infty}$ is 17.82 cm^3 mol^{-1} (*12*). Three sets of measurements, 4, 6, and 7, gave sufficient data to be analyzed by using eq 2; these analyses all agreed with the reported value. Our observed value of 17.80 cm^3 mol^{-1} lies well within the reported range of values and is in excellent agreement with the accepted value, considering the lowest molality at which we made measurements was 0.6520 mol kg^{-1}.

Hydrobromic Acid. For hydrobromic acid only one value for $^{\phi}V^{\infty}$ (25 °C), that of Zen (*14*) of 24.2 cm^3 mol^{-1}, is currently available. This value is calculated from density data in ICT (*13*) and differs slightly from our observed value of 25.07 cm^3 mol^{-1}. Our value does, however, show a better agreement with the accepted value for V^{∞}(ion) of 24.71 cm^3 mol^{-1} at 25 °C for the bromide ion reported by Dunn (*18*) and based on $V^{\infty}(H^+) = 0$ cm^3 mol^{-1}.

Hydriodic Acid. No value for the apparent molar volume at infinite dilution of hydriodic acid has been reported. However, measurements of the density of hydriodic acid solutions have been made by Nishikata et al. (*19*) and show a reasonable agreement with our data. These measurements, however, are quoted only to four decimal places in the density and to one decimal place in the concentration. Also no attempt was made to remove any free iodine present in the solutions. Thus, no accurate comparison or analysis by means of eq 2 was possible. Reasonable agreement is seen, however, between our observed values of 36.37 cm^3 mol^{-1} for $^{\phi}V^{\infty}$ and the value of $V^{\infty}(I^-)$ of 36.22 cm^3 mol^{-1} reported by Dunn (*18*) (again based on $V^{\infty}(H^+) = 0$ cm^3 mol^{-1}.

Perchloric Acid. Excellent agreement is seen between our observed value of 44.10 cm^3 mol^{-1} at 25 °C for $^{\phi}V^{\infty}$ and that of 44.12 cm^3 mol^{-1} reported by Wirth and Collier (*20*).

Acknowledgment

We thank Dr. David J. Turner of the Central Electricity Research Laboratories for his advice and encouragement.

Glossary

A_v	Debye-Hückel slope
M_2	molar mass of solute
m	molality of solute
$^{\phi}V$	apparent molar volume
$^{\phi}V^{\infty}$	apparent molar volume at infinite dilution
$^{\phi}V^{rel}$	$^{\phi}V$(smoothed) − $^{\phi}V^{\infty}$
ρ	density of solution
ρ_0	density of water

Registry No. HCl, 7647-01-0; HBr, 10035-10-6; HI, 10034-85-2; perchloric acid, 7601-90-3.

Literature Cited

(1) Davidson, C. M.; Jameson, R. F. *Chem. Ind.* (*London*) **1963**, 1686.
(2) Vögel, A. I. "A Text Book of Quantitative Inorganic Analysis"; Longman: London, 1951.
(3) Kaye, G. W. C.; Laby, T. H. "Tables of Physical and Chemical Constants"; Longman: London, 1973.
(4) Gibson, R. E.; Loeffler, O.H. *J. Am. Chem. Soc.* **1939**, *61*, 2515.
(5) Kell, G. S. *J. Chem. Eng. Data* **1975**, *20*, 92.
(6) Pitzer, K. S. *J. Phys. Chem.* **1973**, *77*, 268.
(7) Bradley, D. J.; Pitzer, K. S. *J. Phys. Chem.* **1979**, *83*, 1599.
(8) Millero, F. J. *Chem. Rev.* **1971**, *71*, 147.
(9) Redlich, O.; Bigeleisen, J. *J. Am. Chem. Soc.* **1942**, *64*, 758.
(10) Owen, B. B.; Brinkley, S. R. *Ann. N.Y. Acad. Sci.* **1949**, *51*, 753.
(11) Ellis, A. J.; McFadden, I. M. M. *Chem. Commun.* **1968**, 516.
(12) Dunn, L. A. *Trans. Faraday Soc.* **1966**, 62, 2348.
(13) "International Critical Tables"; McGraw-Hill: New York, 1928; Vol. III.
(14) Zen, E-an. *Geochem. Cosmochim. Acta* **1957**, *12*, 103.
(15) Wirth, H. E. *J. Am. Chem. Soc.* **1940**, *62*, 1128.
(16) Geffken, W. *Z. Phys. Chem., Abt. A* **1931**, *A155*, 1.
(17) Gucker, F. T. *Chem.* Rev. **1940**, *13*, 111.
(18) Dunn, L. A. *Trans. Faraday Soc.* **1968**, *64*, 2951.
(19) Nishikata, E.; Ishii, T.; Ohta, T. *J. Chem. Eng. Data* **1981**, *26*, 254.
(20) Wirth, H. E.; Collier, F. N. *J. Am. Chem. Soc.* **1950**, *72*, 5292.

Received for review June 27, 1984. Accepted November 13, 1984. We thank the Science and Engineering Research Council for the award of a studentship to M. R. and CERL for generous support.

Excess Heat Capacities for Mixtures of Benzene with Cyclopentane, Methylcyclohexane, and Cyclooctane at 298.15 K

Reiji Tanaka

Department of Chemistry, Faculty of Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka, Japan

Excess heat capacities were measured by use of a flow calorimeter for binary mixtures of benzene with cyclopentane, methylcyclohexane, and cyclooctane at 298.15 K.

This paper reports excess heat capacities for binary mixtures of benzene with cyclopentane, methylcyclohexane, and cyclooctane at 298.15 K. The measurements were undertaken to provide information about thermodynamic properties of benzene–cycloalkane systems: determinations for the mixture of benzene (1)–cyclohexane (2) which were carried out as a part of the present series have been published previously (*1*).

Experimental Section

The purification of sample liquids were the same as in the previous work (*2*). The mixtures were prepared with specially devised vessels (*3*), and the error in composition x was less than 2×10^{-5}.

The heat capacities C_p were determined relative to that of the reference liquid by using a Picker flow calorimeter (Techneurop Inc., Montreal, Canada). Examinations and the improved operation for this apparatus have been described previously (*1*). The volumetric heat capacities (C_p/V), the heat capacity divided by the volume, were determined from the values of the effective power of heating P dissipated to the flowing liquids, the power change ΔP due to the change of C_p/V in the working cell tube, and the value of C_p/V of the reference liquid. In order to cancel the boundary effects (*1*) a pair of ΔP was taken by reversing the sequence of the liquids to be flowed, and C_p/V was calculated by the equation

$$(C_p/V)_s = (C_p/V)_r\{1 + \Delta P(r\rightarrow s)/P\}^{1/2}/\{1 + \Delta P(s\rightarrow r)/P\}^{1/2} \quad (1)$$

where the suffixes r and s indicate reference and sample liquid, respectively. Liquids were flowed at a rate of 0.013 cm^3·s^{-1} and heated with a temperature increment of 1 K. The liquid temperatures were centered on 298.15 ± 0.01 K. *n*-Heptane was used as the standard for the determinations: the adopted

0021-9568/85/1730-0267$01.50/0