

**Table III. Parameters of the Refractive Index–Mole Fraction Isotherms**

Temp, °C	Composition range (mol %, Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O)	$n = a - bx$		
		$a$	$10b$	$10^3SE$
25.0	0.0–39.4	1.4869	0.182	0.29
	39.4–100.0	1.4902	0.261	0.25
50.0	0.0–39.4	1.4830	0.179	0.24
	39.4–100.0	1.4863	0.261	0.13
75.0	0.0–39.4	1.4795	0.186	0.05
	39.4–100.0	1.4825	0.258	0.12

shown as a function of composition in Figure 2. A value of 37.47 for the molar polarization ( $P_{LL}$ ) of Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O at 25 °C could be favorably compared with the value 38 estimated from the molar polarization values for Ca(NO<sub>3</sub>)<sub>2</sub>·4.1H<sub>2</sub>O + KNO<sub>3</sub> mixtures reported by Rao et al. (7).

The molar refractions have been evaluated by several empirical formulas (7) of which only the Lorenz–Lorentz relation appears to have a sound theoretical basis. However, Young and Finn (9) have shown that the Gladstone–Dale formula

$$P_{GD} = (n - 1)(M/\rho)$$

is quite adequate in giving temperature-independent molar refractions. If the molar polarizations were temperature independent, then the differential form of Gladstone–Dale and Lorenz–Lorentz equations would provide a direct relation between the coefficient of thermal expansion,  $\alpha$ , and the temperature dependence of refractive index through the expressions

$$\left[ \frac{1}{(n - 1)} \right] \frac{dn}{dT} = \frac{1}{\rho} \frac{d\rho}{dT} = \alpha_{GD} \quad (3)$$

$$\left[ \frac{6n}{(n^2 - 1)(n^2 + 2)} \right] \frac{dn}{dT} = \frac{1}{\rho} \frac{d\rho}{dT} = \alpha_{LL} \quad (4)$$

Computed values of  $\alpha_{GD}$  and  $\alpha_{LL}$  for all the mixtures are recorded in Table II. These are found to be smaller than the directly measured values of expansivities ( $\alpha$ ), the discrepancy being greater for  $\alpha_{LL}$  than for  $\alpha_{GD}$ . A similar observation has been made by Rao et al. (7) while analyzing their results on Ca(NO<sub>3</sub>)<sub>2</sub>·4.1H<sub>2</sub>O + KNO<sub>3</sub> mixtures. For the mixtures investigated in this study, the ratio  $\alpha/\alpha_{GD}$  lies between 1.5 and 1.9, which is much higher than the value 1.15 reported by Rao et al. (7) for the Ca(NO<sub>3</sub>)<sub>2</sub>·4.1H<sub>2</sub>O + KNO<sub>3</sub> system. It may be that due to the "release" of water from the coordination of trivalent chromium ion by NO<sub>3</sub><sup>-</sup>, the thermal expansivity of this system is increased and is thus reflected in the ratio  $\alpha/\alpha_{GD}$ .

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## Heats of Mixing of Binary Chloroalkane–*n*-Alkane and Chloroalkane–*n*-Alcohol Systems at 25 °C

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**Heats of mixing of six binary chloroalkane–*n*-alkane and nine chloroalkane–*n*-alcohol systems were measured in an isothermal dilution calorimeter. Experimental results expressed as  $\Delta H/x_1x_2$  vs.  $x_1$  were interpolated using the expanded spline-fit technique. Heats of mixing are reported at regular composition intervals.**

Accurate heat-of-mixing data are extremely valuable for testing solution models. In order to understand the effect of molecular structure on thermodynamic properties of solutions, systematic information covering components of different structural characteristics is required. This work presents heats of mixing data for chloroalkanes with different *n*-alkanes and *n*-alcohols. Data on these systems are scarce in the literature. Only data for three chloroalkane–*n*-alkane systems have been previously reported (3). Measurements in this study were made at 25 °C.

† Deceased July 1976.

#### Materials and Apparatus

Materials used in this work, together with their suppliers and specifications, are listed in Table I. Refractive indices of the pure components were measured in a Bausch & Lomb refractometer. Experimental and literature values of the index of refraction are also presented in Table I. The agreement between experimental and literature values of the index of refraction was considered satisfactory and the materials were used without further purification.

The heats of mixing measurements were made in an isothermal semicontinuous dilution calorimeter of Van Ness type (6) specially constructed to measure heats of mixing of endothermic systems. The basic features of this calorimeter have been described elsewhere (5). The principle of operation of the calorimeter is as follows: one component is introduced semicontinuously, at constant temperature and pressure, into a cell initially containing the other component. Electrical energy is added to the system in order to maintain the temperature constant during the mixing process. The amount of energy added is a measure of the heat of mixing. The entire heat of

Table I. Materials Employed

Material	Supplier and specification	Refractive index			$T, ^\circ\text{C}$
		Exptl	Lit.	Source of lit.	
<i>n</i> -Hexane	Phillips Petroleum Co., pure grade, 99* mol %	1.3725	1.372 26	1	25
<i>n</i> -Octane		1.3954	1.395 05	1	25
<i>n</i> -Nonane		1.4034	1.403 11	1	25
<i>n</i> -Butyl alcohol	Aldrich Chemical Co., 99 mol %	1.3970	1.397 3	1	25
<i>n</i> -Pentyl alcohol		1.4079	1.408 1	1	25
<i>n</i> -Octyl alcohol		1.4276	1.427 5	1	25
<i>n</i> -Heptyl alcohol	Matheson Coleman & Bell, 99* mol %	1.4240	1.424 9	2	20
1-Chlorobutane	Chemical Samples Co., 99 mol %	1.4014	1.401 59	2	20
2-Chlorobutane	Aldrich Chemical Co., 99* mol %	1.3950	1.397 09	2	20
1-Chlorooctane	Aldrich Chemical Co., 99* mol %	1.42980	1.430 58	2	20

Table II. Systems Studied at 25 °C

System	Abbreviation
Chloroalkane- <i>n</i> -Alkane Systems	
1-Chlorobutane- <i>n</i> -hexane	1-C <sub>4</sub> Cl/ <i>n</i> -C <sub>6</sub>
1-Chlorobutane- <i>n</i> -nonane	1-C <sub>4</sub> Cl/ <i>n</i> -C <sub>9</sub>
2-Chlorobutane- <i>n</i> -hexane	2-C <sub>4</sub> Cl/ <i>n</i> -C <sub>6</sub>
2-Chlorobutane- <i>n</i> -octane	2-C <sub>4</sub> Cl/ <i>n</i> -C <sub>8</sub>
1-Chlorooctane- <i>n</i> -hexane	1-C <sub>8</sub> Cl/ <i>n</i> -C <sub>6</sub>
1-Chlorooctane- <i>n</i> -octane	1-C <sub>8</sub> Cl/ <i>n</i> -C <sub>8</sub>
Chloroalkane- <i>n</i> -Alcohol Systems	
1-Chlorobutane- <i>n</i> -Butyl alcohol	1-C <sub>4</sub> Cl/ <i>n</i> -C <sub>4</sub> OH
1-Chlorobutane- <i>n</i> -Heptyl alcohol	1-C <sub>4</sub> Cl/ <i>n</i> -C <sub>7</sub> OH
1-Chlorobutane- <i>n</i> -Octyl alcohol	1-C <sub>4</sub> Cl/ <i>n</i> -C <sub>8</sub> OH
2-Chlorobutane- <i>n</i> -Pentyl alcohol	2-C <sub>4</sub> Cl/ <i>n</i> -C <sub>5</sub> OH
2-Chlorobutane- <i>n</i> -Heptyl alcohol	2-C <sub>4</sub> Cl/ <i>n</i> -C <sub>7</sub> OH
2-Chlorobutane- <i>n</i> -Octyl alcohol	2-C <sub>4</sub> Cl/ <i>n</i> -C <sub>8</sub> OH
1-Chlorooctane- <i>n</i> -Butyl alcohol	1-C <sub>8</sub> Cl/ <i>n</i> -C <sub>4</sub> OH
1-Chlorooctane- <i>n</i> -Pentyl alcohol	1-C <sub>8</sub> Cl/ <i>n</i> -C <sub>5</sub> OH
1-Chlorooctane- <i>n</i> -Octyl alcohol	1-C <sub>8</sub> Cl/ <i>n</i> -C <sub>8</sub> OH

mixing curve is obtained in two runs. In the second run the two components are interchanged. In order to avoid errors due to vaporization-condensation effects, this type of calorimeter must be operated with no vapor space in the cell. The performance of the calorimeter has been periodically checked by measurements of the standard system benzene-cyclohexane at 25 °C. Its accuracy is believed to be within 1%.

### Experimental Results and Conclusions

Experimental measurements were made at 25 °C for six binary chloroalkane-*n*-alkane and nine chloroalkane-*n*-alcohol

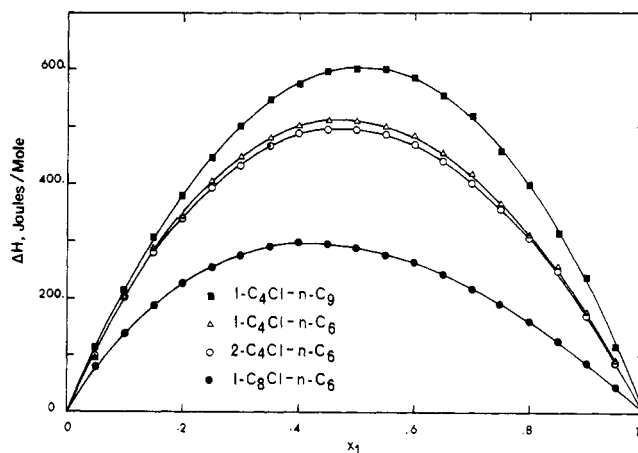


Figure 1. Heats of mixing at 25 °C for some chloroalkane-*n*-alkane systems, J/mol.

systems. Table II shows the binary systems studied and the abbreviated form used from here on to represent them. No less than 50 experimental points were measured for each system. The original data, too extensive to be reproduced here, have been filed with the National Depository of Unpublished Data, National Science Library, National Research Council of Canada, Ottawa, Ontario, Canada.

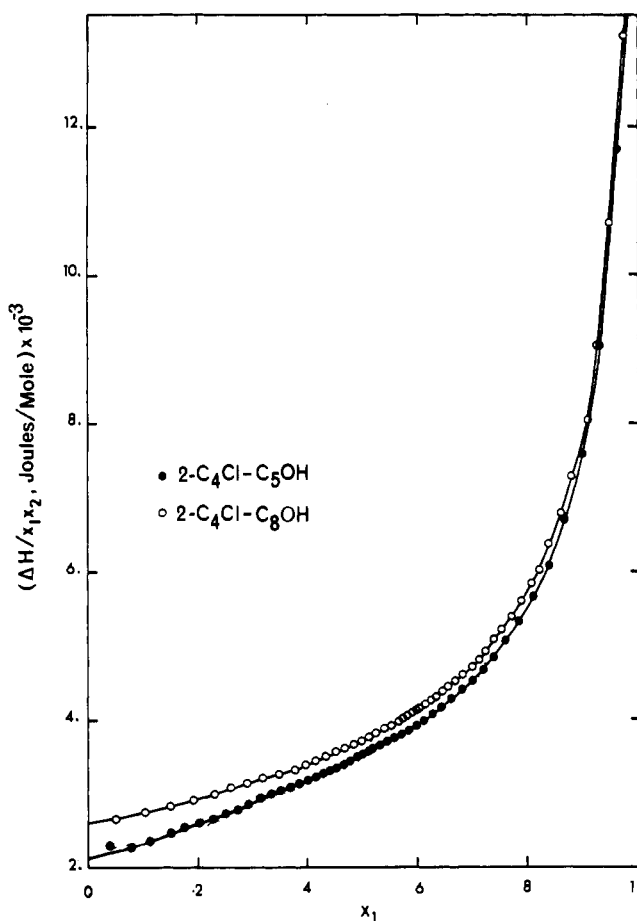
The expanded spline-fit technique (4) was used to represent the experimental values of  $\Delta H/x_1x_2$  vs.  $x_1$ . Interpolated values of  $\Delta H/x_1x_2$  from spline fits at regular intervals of composition were reconverted to heats of mixing and are presented in Table

Table III. Heats of Mixing for Chloroalkane (1)-*n*-Alkane (2) Systems at 25 °C ( $\Delta H, \text{J/mol}$ )

$x_1$	1-C <sub>4</sub> Cl/ <i>n</i> -C <sub>6</sub>	1-C <sub>4</sub> Cl/ <i>n</i> -C <sub>9</sub>	1-C <sub>8</sub> Cl/ <i>n</i> -C <sub>6</sub>	1-C <sub>8</sub> Cl/ <i>n</i> -C <sub>8</sub>	2-C <sub>4</sub> Cl/ <i>n</i> -C <sub>6</sub>	2-C <sub>4</sub> Cl/ <i>n</i> -C <sub>8</sub>
0.05	110.3	113.3	76.8	78.1	106.2	110.9
0.10	204.8	214.8	137.5	142.8	197.3	208.7
0.15	285.1	304.5	186.3	195.5	274.6	294.0
0.20	352.0	382.2	225.4	239.2	339.2	367.0
0.25	405.9	448.1	255.6	274.3	391.5	428.4
0.30	447.9	502.5	277.0	301.4	432.6	478.6
0.35	479.8	545.3	292.1	320.6	463.2	517.8
0.40	501.6	576.5	300.2	331.9	483.6	546.0
0.45	512.1	596.0	297.5	337.1	494.0	563.6
0.50	511.3	603.8	289.0	333.8	495.0	570.5
0.55	502.2	599.5	278.4	318.8	487.1	567.0
0.60	481.9	583.2	262.8	305.3	469.7	551.3
0.65	453.4	555.1	242.5	284.4	440.9	524.2
0.70	415.4	514.7	218.2	258.9	403.8	485.5
0.75	368.6	463.3	190.3	228.0	358.3	435.2
0.80	313.3	399.2	159.0	192.0	303.8	373.0
0.85	248.9	322.2	124.4	150.6	240.7	299.0
0.90	175.2	230.2	86.4	105.6	169.1	212.8
0.95	92.3	122.7	45.0	55.1	89.0	113.4

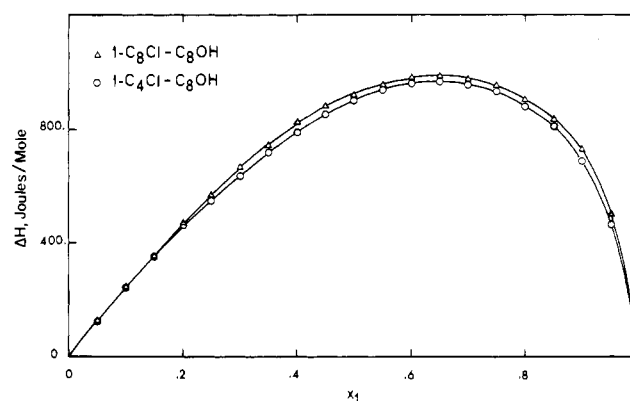
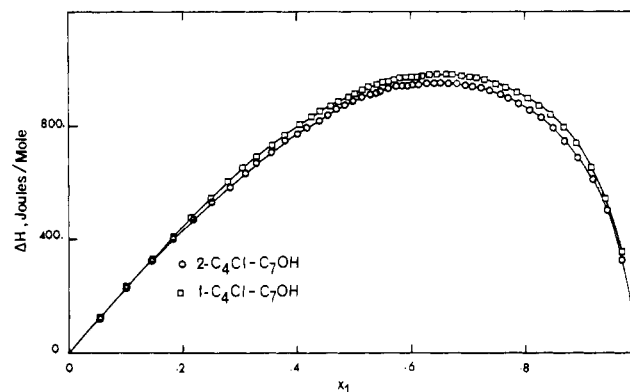
Table IV. Heats of Mixing for Chloroalkane (1)-*n*-Alcohol (2) Systems at 25 °C ( $\Delta H$ , J/mol)

$x_1$	1-C <sub>4</sub> Cl/ <i>n</i> -C <sub>4</sub> OH	1-C <sub>4</sub> Cl/ <i>n</i> -C <sub>7</sub> OH	1-C <sub>4</sub> Cl/ <i>n</i> -C <sub>8</sub> OH	1-C <sub>8</sub> Cl/ <i>n</i> -C <sub>4</sub> OH	1-C <sub>8</sub> Cl/ <i>n</i> -C <sub>5</sub> OH	1-C <sub>8</sub> Cl/ <i>n</i> -C <sub>8</sub> OH	2-C <sub>4</sub> Cl/ <i>n</i> -C <sub>5</sub> OH	2-C <sub>4</sub> Cl/ <i>n</i> -C <sub>7</sub> OH	2-C <sub>4</sub> Cl/ <i>n</i> -C <sub>8</sub> OH
0.05	93.0	112.2	118.9	130.8	125.4	122.4	107.3	118.3	127.2
0.10	189.4	225.1	233.6	259.0	250.9	243.5	210.0	232.4	247.6
0.15	274.4	331.6	343.4	384.9	375.0	359.2	315.9	342.2	362.0
0.20	384.3	430.6	447.4	505.3	493.4	468.2	421.1	447.0	470.4
0.25	479.4	524.6	544.9	614.6	602.1	569.8	517.3	545.8	571.1
0.30	570.6	614.9	635.0	717.4	708.1	662.1	606.7	637.6	663.8
0.35	654.3	697.5	716.8	807.2	787.6	744.2	691.4	720.7	747.1
0.40	729.6	768.5	789.1	892.6	859.9	818.6	767.3	794.2	820.1
0.45	797.9	830.6	850.7	937.3	901.6	875.7	829.9	857.8	882.1
0.50	847.3	885.5	900.0	986.0	944.5	918.5	881.0	912.0	933.5
0.55	894.5	918.5	937.3	1041.5	1007.8	951.4	923.2	948.9	969.7
0.60	920.4	942.7	958.8	1068.7	1037.3	957.8	933.4	977.5	995.3
0.65	922.3	943.0	965.1	1057.7	1022.4	991.5	958.0	980.0	1005.8
0.70	929.7	934.3	956.6	1028.6	987.2	994.6	971.3	973.0	985.5
0.75	919.9	926.4	927.9	995.6	948.6	947.8	930.8	946.7	978.0
0.80	856.3	865.1	880.0	959.4	909.1	890.9	868.6	895.7	921.9
0.85	769.8	778.6	800.8	901.0	852.7	835.5	804.7	811.4	827.5
0.90	669.2	675.8	677.6	777.0	737.3	746.1	711.2	711.4	720.1
0.95	475.7	476.0	476.3	513.2	489.2	525.3	498.5	507.9	518.4

Figure 2.  $\Delta H/x_1x_2$  at 25 °C for the systems 2-chlorobutane-*n*-pentyl alcohol and 2-chlorobutane-*n*-octyl alcohol, J/mol.

III for chloroalkane-*n*-alkane systems and in Table IV for chloroalkane-*n*-alcohol systems. Figures 1-4 present the data for some typical systems. It can be seen from Figures 2 and 4 that all the data lie on smooth curves and it is well described by the spline-fitted curves. Figures 1 and 3 present the smoothed curves and the interpolated points.

From Tables II and IV and Figures 1-4, some conclusions can be drawn about the effect of molecular structure on heat of mixing. Figure 1 represents some chloroalkane-*n*-alkane systems of Table III. It can be seen that for the systems studied the increase of the alkane chain length causes an increase in the heat of mixing for the same chloroalkane at the same

Figure 3. Heats of mixing at 25 °C for the systems 1-chlorooctane-*n*-octyl alcohol and 1-chlorobutane-*n*-octyl alcohol, J/mol.Figure 4. Heats of mixing at 25 °C for the systems 1-chlorobutane-*n*-heptyl alcohol and 2-chlorobutane-*n*-heptyl alcohol, J/mol.

composition. However, an increase in the chloroalkane chain length causes a decrease in the heat of mixing. The change in the position of the Cl atom from carbon one to carbon two decreases the heat of mixing. It is interesting to compare the systems, 1-C<sub>4</sub>Cl/*n*-C<sub>9</sub> and 2-C<sub>4</sub>Cl/*n*-C<sub>9</sub>. In this case the effects of changing the hydrocarbon chain length by one CH<sub>2</sub> group and the position of the substitution of the Cl atom tend to compensate as expected. However, the effect of the change in the position of the Cl atom appears to be dominant.

Figures 2, 3, and 4 represent some chloroalkane-*n*-alcohol systems of Table IV. Figure 2 shows the effect of increasing the alcohol chain length for two 2-chlorobutane systems. In general, for 1-chlorobutane and 2-chlorobutane systems, an increase in the alcohol chain length increases the heat of mixing.

However for 1-chlorooctane systems, the effect of increasing the alcohol chain length from C<sub>4</sub> to C<sub>8</sub> is the opposite.

Finally, Figures 3 and 4 show that both the increase in the chloroalkane chain length and the change of the position of the Cl atom from C1 to C2 increase the heat of mixing for the chloroalkane-*n*-alcohol systems.

#### Acknowledgment

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#### Glossary

$x$	mole fraction
$\Delta H$	heat of mixing per mole of mixture, J/mol

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## Isochoric Pressure-Volume-Temperature Measurements for Compressed Liquid Propane

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Isochoric *P-V-T* measurements have been made on compressed liquid propane using a newly constructed Invar cell. The results, which are nearly perfectly isochoric, cover a previously unexplored portion of propane's *P-V-T* surface, viz., densities from  $\sim 0.65$  to  $\sim 0.51$  g/cm<sup>3</sup>, temperatures from 165 to 325 K, and pressures extending to  $\sim 42$  MPa (6000 psia). The results are tabulated as pseudoisochores and as adjusted true isochores in Table I.

There have been numerous studies of the volumetric behavior of liquid and gaseous propane as recently documented by

Goodwin (1). None of these studies, unfortunately, extended substantially into the cryogenic region of the phase diagram. Due to the practical importance of this region in LNG density calculations, a study has been undertaken to investigate propane *P-V-T* behavior below 325 K by an apparatus and technique discussed previously (2). The subject of the studies selected was Phillips Petroleum research grade propane (99.98%) whose purity was substantiated.

The results of this study are given as smoothed pseudoisochores in Table I, columns 1, 2, and 3. Columns 3 and 4, on the other hand, represent values of temperature and pressure corresponding to the fixed isochoric values tested in the fourth column of the same table. Uncertainties in the densities are

Table I. Smoothed Pseudoisochores and Isochores for Liquid Propane

$p$ , MPa (at pseudoisochore)	$\rho$ , g/cm <sup>3</sup>	$T$ , K	$p$ , MPa (at isochore)	$p$ , MPa (at pseudo- isochore)	$\rho$ , g/cm <sup>3</sup>	$T$ , K	$p$ , MPa (at isochore)
0.70326	0.651 60	166.227	0.70326	20.685	0.651 39	178.373	$\rho = 0.651$ 60
2.7642	0.651 58	167.461	2.7963	27.411	0.651 32	182.557	21.052
4.9045	0.651 56	168.747	4.9694	35.720	0.651 24	187.796	27.916
8.7235	0.651 52	171.053	8.8563	38.892	0.651 21	189.817	26.394
14.279	0.651 46	174.434	14.517				39.632
			$\rho = 0.640$ 50				$\rho = 0.640$ 50
1.3550	0.640 48	177.351	1.3841	21.735	0.640 27	190.854	22.104
5.1280	0.640 44	179.819	5.2167	27.561	0.640 21	194.795	28.039
7.7509	0.640 41	181.543	7.8855	33.593	0.640 15	198.915	34.186
10.459	0.640 39	183.330	10.626	37.250	0.640 11	201.433	37.922
17.313	0.640 32	187.888	17.596	41.844	0.640 06	204.618	42.619
			$\rho = 0.632$ 34				$\rho = 0.632$ 34
0.61631	0.632 34	184.715	0.61631	19.735	0.632 14	198.151	20.031
2.4300	0.632 32	185.973	2.4571	27.955	0.632 05	204.051	28.403
4.2992	0.632 30	187.723	4.3541	34.147	0.631 99	208.548	34.704
8.1375	0.632 26	189.954	8.2489	41.214	0.631 91	213.736	41.922
15.111	0.632 19	194.865	15.328				