Table II. Resistivity and Temperature Coefficient of Pure Molybdenum

Material Investigated	Resistivity ($\mu\,\Omega$ Cm.) 0° C.	25° C.	T. C. α., 0° – 100° C. (Degree^{-1})	$\alpha\,\rho(25^\circ)$ ($10^{-10}\,\Omega$ Cm. Degree^{-1})	Lit. Reference
Single crystal wire	5.03	5.62	0.00473	266	(*1*)
Pure Mo			0.00459		(*1*)
Pure single crystal	5.05	5.65	0.00476	269	(2)
Wire	...	...	0.00459		(8)
Wire, 99.85%	5.17	5.77	0.00462	266	(5)
Wire, 99.85%	5.25	5.85	0.00461	270	(5)
Spectroscop. standard rod, Johnson-Matthey	5.05	5.65	0.00475	268	(7)
Zone purified rod, 99.999% pure	5.00	5.57	0.00482	268	Authors

RESULTS

The experimental resistivity values are shown in column 2 of Table I. A linear approximation of the resistivity as a function of temperature has been calculated from the experimental data, applying the least squares method over the interval 0° to 100° C.:

$$\rho(T) = \rho_o + \alpha\rho_o T \qquad (2)$$

The average temperature coefficient of resistivity in this range was thus α = 0.00482 per centigrade. Equation 2 was then used to calculate the resistivity values which are shown in column 3 of Table I. The differences between measured and calculated values listed in the last column indicate that the true temperature function is not linear, which is reflected clearly if all experimental data are plotted graphically. This behavior is to be expected since molybdenum has a relatively high Debye temperature of 360° to 380° C. (*6*).

A comparison of resistivities and temperature coefficients published by various authors is shown in Table II. The data of this investigation indicate the highest purity of molybdenum which has been reported so far. This is confirmed by the resistance ratio

$$\frac{R\,(-196^\circ\,C.)}{R\,(0^\circ\,C.)} = 0.097 \pm 1\%$$

For comparison, Kannuluik reported ratios of 0.1814 and 0.1705 for two molybdenum wires at the two temperatures −183° and 0° C.

As shown in the next to last column of Table II, Mathiessen's Rule is valid for all molybdenum samples of reasonably good purity. According to Geiss and van Liempt (*2*), this is also true for drawn wires with a considerable degree of cold deformation.

LITERATURE CITED

(1) Geiss, W., van Liempt, J.A.M., *Z. Metallk.* **17**, 194 (1925).
(2) Geiss, W., van Liempt, J.A.M., *Z. Physik* 41, 867 (1927).
(3) "Gmelins Handbuch der Anorg. Chemie," 8th ed. p. 44, 1935.
(4) Harwood, J., Ed., "The Metal Molybdenum," p. 10, Am. Soc. Metals, Cleveland, Ohio, 1958.
(5) Kannuluik, W.G., *Proc. Roy. Soc. London* **A 141**, 159 (1933).
(6) Meissner, W., Voigt, B., *Ann. Physik (5)*, **7**, 911 (1930).
(7) Tye, R.P., "Report on Conference on Nb, Ta, Mo, W" in Sheffield, p. 169, Elvesier, Amsterdam, 1961.
(8) Zwikker, C., *Physica* **7**, 71 (1927).

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Volume Changes of Mixing of Some Ethanol-Hydrocarbon Systems

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Volume changes of mixing at 25° and 45° C. are reported for the liquid binary systems made up of ethanol with cyclohexane, toluene, o-xylene, *m*-xylene, and *p*-xylene.

PRECISE measurements have been made of the volume changes of mixing at 25° and 45° C. for binary liquid systems consisting of ethanol with cyclohexane, toluene, *o*-xylene, *m*-xylene, and *p*-xylene. The apparatus used consisted of a dilatometer, which is fully described elsewhere (*4*). It followed the general design of the apparatus described by Anderson (*1*), but incorporated several modifications. The purities of the materials used are indicated in Table I.

To test the results obtained with this dilatometer for agreement with those obtained by earlier investigators, data were first obtained for the carbon tetrachloride–cyclohexane system at 30° C. The excellence of agreement is shown in Figure 1.

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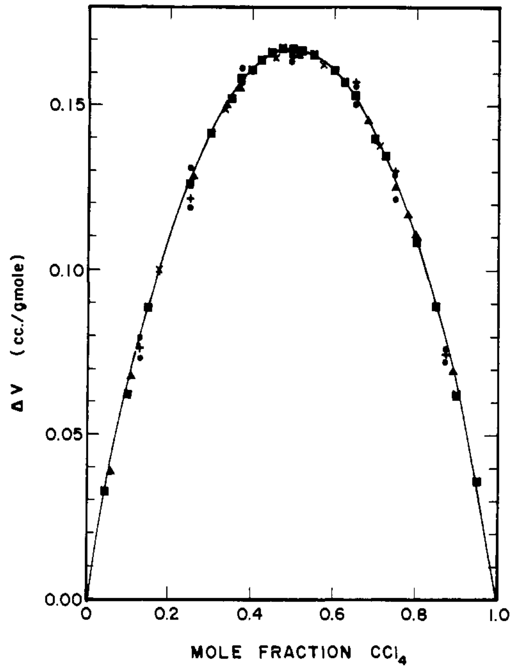

Figure 1. Volume changes of mixing for the carbon tetrachloride–cyclohexane system at 30° C.

- ■ This investigation
- ● Wood and Grey (7)
- + Reddy, Subrahmanyan, and Bhimasenachar (5)
- X Desmyter and van der Waals (2)
- ▲ Anderson (1)

Table I. Materials

Cyclohexane	Certified, Fisher Scientific Co. Trace impurities only[a]
Ethanol	Reagent quality, 200 proof, U. S. Industrial Chemicals. Trace impurities only[a]
Toluene	Certified, Fisher Scientific Co. Trace impurities only[a]
o-Xylene	99 mole %, Phillips Petroleum Co. Contains approximately 0.75 mole % *p*-xylene[b]
p-Xylene	99 mole %, Phillips Petroleum Co. Contains less than 0.15 mole % *o*-xylene and 0.2 mole % toluene[b]
m-Xylene	99 mole %, Phillips Petroleum Co. Trace impurities only[b]

[a] By chromatographic analysis. [b] The xylenes were washed with mercury for 1 to 2 hours and filtered to remove small amounts of sulfur compounds, which otherwise attacked the mercury in the dilatometer.

Table II. Volume Change of Mixing

$\Delta V/x_1x_2$ in cc./gram mole

Mole Fraction, Ethanol	Ethanol-Cyclohexane 25° C.	45° C.	Mole Fraction, Ethanol	Ethanol-Cyclohexane 25° C.	45° C.
0.000	8.675	11.000	0.125	2.992	3.868
0.005	7.492	10.155	0.150	2.861	3.635
0.010	6.208	9.363	0.175	2.745	3.460
0.015	5.439	8.626	0.200	2.644	3.322
0.020	4.961	7.943	0.300	2.379	2.948
0.025	4.626	7.319	0.400	2.277	2.751
0.030	4.363	6.767	0.500	2.265	2.683
0.035	4.147	6.298	0.600	2.313	2.690
0.040	3.977	5.915	0.700	2.420	2.751
0.045	3.842	5.619	0.800	2.577	2.874
0.050	3.731	5.385	0.900	2.763	3.048
0.075	3.370	4.655	1.000	2.990	3.260
0.100	3.152	4.190			

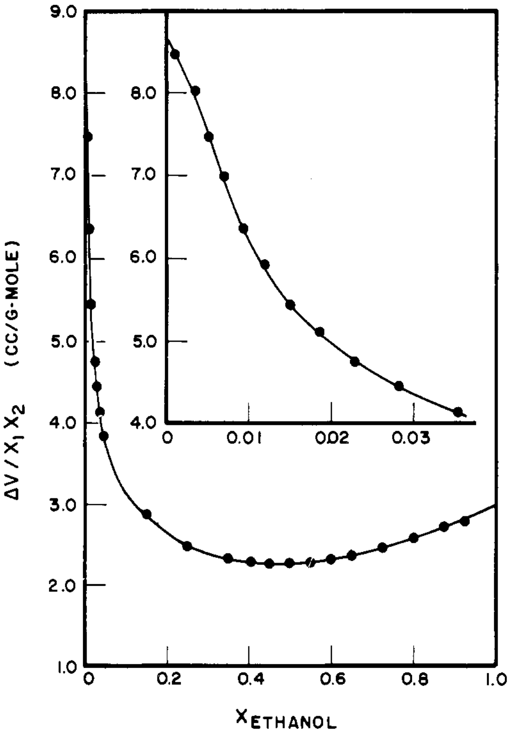

Figure 2. Volume changes of mixing for the ethanol-cyclohexane system at 25° C.

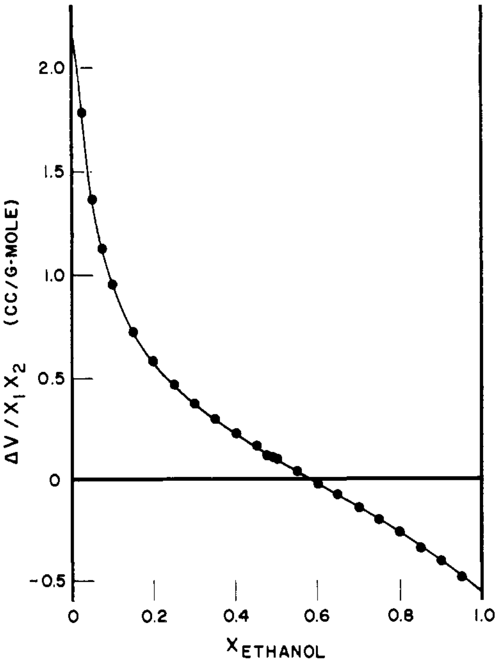

Figure 3. Volume changes of mixing for the ethanol-*m*-xylene system at 25° C.

Table III. Volume Change of Mixing

$\Delta V/x_1x_2$ in cc./gram mole

Mole Fraction, Ethanol	Ethanol-Toluene		Ethanol-*o*-Xylene		Ethanol-*m*-Xylene		Ethanol-*p*-Xylene	
	25° C.	45° C.	25° C.	45° C.	25° C.	45° C.	25° C.	45° C.
0.000	1.495	2.389	1.807	3.036	2.178	2.947	1.298	2.471
0.025	1.163	2.111	1.558	2.514	1.778	2.523	1.140	2.192
0.050	0.814	1.790	1.251	1.994	1.357	2.111	0.945	1.900
0.075	0.629	1.492	0.966	1.667	1.117	1.865	0.773	1.608
0.100	0.500	1.266	0.780	1.440	0.949	1.630	0.660	1.413
0.150	0.311	0.954	0.547	1.126	0.720	1.321	0.490	1.125
0.200	0.192	0.754	0.373	0.913	0.574	1.115	0.370	0.933
0.300	0.007	0.487	0.172	0.616	0.371	0.833	0.176	0.658
0.400	−0.146	0.301	−0.002	0.408	0.220	0.644	0.026	0.456
0.500	−0.280	0.138	−0.146	0.230	0.094	0.486	−0.108	0.286
0.600	−0.419	−0.022	−0.281	0.070	−0.033	0.349	−0.245	0.132
0.700	−0.574	−0.185	−0.418	−0.092	−0.150	0.214	−0.392	−0.026
0.800	−0.747	−0.352	−0.576	−0.275	−0.269	0.075	−0.563	−0.208
0.900	−1.000	−0.553	−0.777	−0.488	−0.412	−0.088	−0.771	−0.409
1.000	−1.400	−0.783	−1.040	−0.760	−0.560	−0.289	−1.035	−0.638

The remaining results of this work are presented in Tables II and III. The values of $\Delta V/x_1x_2$ given in these tables at even values of ethanol mole fraction were interpolated from the experimental data by machine computation through use of the spline-fit technique (*3*). In the course of this computational procedure, the second derivative, $\partial^2\Delta V/\partial x_1^2$, determined by the spline-fit was evaluated at each data point. For an occasional point, this calculated second derivative was inconsistent with the general trend. Such points were rejected, and the spline-fit procedure was again applied to the remaining points. The agreement of the curves determined by the spline-fit interpolated values with the experimental data is illustrated in Figures 2 and 3.

The spline-fit technique forces the smoothing function through every experimental point which it does not reject, and can be used successfully only when the data lie on a very smooth curve. Thus it is not possible to report any meaningful statistical measure of the deviation of data points from the smoothing function. On the basis of agreement of results with those of other reliable investigators, of the reproducibility of runs, and of the propagation of measurement errors, the authors' results are believed to be accurate within ±1%.

The values of $\Delta V/x_1x_2$ at $x_1 = 0$ and at $x_1 = 1$ are finite but indeterminate. They also represent $\overline{\Delta V_1}$ and $\overline{\Delta V_2}$ at infinite dilution. Since they must be determined by extrapolation, they are subject to some uncertainty. Extrapolation to $x_1 = 0$ for the ethanol-cyclohexane system is particularly difficult because the $\Delta V/x_1x_2$ *vs.* x_1 curve rises very steeply to high values in the vicinity of $x_1 = 0$. For this system, dilution runs were made in which a solution of ethanol in cyclohexane was injected into cyclohexane so as to obtain data at mole fractions as low as $x_1 = 0.001$. The resulting data are illustrated in Figure 2.

The data listed in Tables II and III are adequate to allow the preparation of graphs of $\Delta V/x_1x_2$ *vs.* x_1 over the complete composition range. Accurate values of the partial molal properties, $\overline{\Delta V_1}$ and $\overline{\Delta V_2}$, are readily calculated from such graphs by the method described by Van Ness (*6*).

The primary purpose of this paper is the disclosure of data and not the interpretation of results in terms of molecular interactions. It will suffice here to point out a few major trends indicated by the data. The measured volume changes are quite small in comparison with the molal volumes of the solutions. In no case did the volume change of mixing amount to as much as 1% of the molal volume, and for the ethanol-aromatic systems, this figure was always less than 0.2%. For all systems studied, over the complete composition range the volume changes of mixing increased appreciably (in the algebraic sense) with an increase in temperature from 25° to 45° C.

The difference in behavior of the ethanol-cyclohexane system as contrasted with the ethanol-aromatic systems is striking. For the ethanol-cyclohexane system, ΔV is positive at all compositions, whereas the alcohol-aromatic systems all exhibit regions of both positive and negative volume changes. The partial molal volume change of mixing of ethanol in an infinitely dilute ethanol solution is some five times larger for the cyclohexane system than for the aromatic systems. The large partial volume changes for ethanol at high dilution in cyclohexane certainly arise because of the breaking of hydrogen bonds between ethanol molecules. This also occurs in the aromatic systems, but the effect on the volume change is evidently largely counteracted by a strong interaction between ethanol molecules and the benzene ring structure. Some such interaction presumably also causes the volume changes of mixing to become negative in ethanol-aromatic systems at higher ethanol concentrations. The molecular interactions in these systems are probably much too complex to interpret with any confidence from volume change data alone. However, such data certainly provide vital information for the testing of theories of solutions.

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LITERATURE CITED

(1) Anderson, Ralph, Ph.D. thesis, University of California at Berkeley, 1961.

(2) Desmyter, A., van der Waals, J.H., *Rec. Trav. Chim.* **77**, 53 (1958).

(3) Landis, F., Nilson, E.N., "Progress in International Research on Thermodynamic and Transport Properties," p. 218, Academic Press, New York, 1962.

(4) Pardo, F., M.Ch.E. thesis, Rensselaer Polytechnic Institute, Troy, N. Y., 1964.

(5) Reddy, K.C., Subrahmanyan, S.V., Bhimasenachar, J., *J. Phys. Soc. Japan* **19**, 559 (1964).

(6) Van Ness, H.C., "Classical Thermodynamics of Non-Electrolyte Solutions," p. 100, Macmillan, New York, 1964.

(7) Wood, S.E., Gray, J.A., *J. Am. Chem. Soc.* **74**, 3729 (1952).

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