Viscosity of Some Ternary Liquid Nonelectrolyte Mixtures

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Viscosities, densities, excess Gibbs free energies of activation of flow, and excess volumes are reported for mixtures of 11 ternary nonelectrolyte systems at 25° C. from among the components: n-hexadecane, n-tetradecane, n-hexane, 2-bromobutane, carbon tetrachloride, benzene, and 4-methylcyclohexanone. Experimental viscosities are compared with values obtained by fitting the data by the approaches of Kalidas and Laddha and an extension of that of Katti and Chaudhri, both based on the Eyring viscosity equation. The first approach produces a standard error of 0.3 to 1.3%; the second, 0.3 to 0.5%. Both tend toward better representation of the data than that obtained by fitting viscosity directly with a power series in mole fraction. For one system, hexadecane-tetradecane-hexane, the principle of congruence is applied to predicting the viscosity, with a standard error of 1.3%, less than one tenth that of several equations commonly used in predicting viscosities of mixtures. The excess Gibbs free energy of activation of flow and the excess volumes are compared with values previously reported for the binary subsystems. Both excess properties are fitted by power series equations in mole fraction. The former is represented to a standard error of from 2 to 7 cal. per mole, and the latter to 0.01 to 0.06 ml. per mole. Correlation between the predicted algebraic signs of the excess volume and the excess Gibbs free energy of activation of flow is poor in terms of a presumed dominance of free volume effects in governing viscosity.

THE LITERATURE OF VISCOSITY in multicomponent systems of nonaqueous nonelectrolytes is rather limited, except for a number of systems of commercially significant hydroxyl-containing components. Recently (*8*), viscometric behavior in a series of 14 binary nonelectrolyte systems was described. The components varied in molecular size from one to 16 carbons, and some systematic effects were evident. That work has now been extended to include 11 ternary systems composed of the previous binary subsystems:

I. *n*-Hexadecane–*n*-hexane–2-bromobutane
II. *n*-Hexadecane–benzene–*n*-hexane
III. *n*-Hexadecane–carbon tetrachloride–benzene
IV. *n*-Hexadecane–carbon tetrachloride–*n*-hexane
V. *n*-Hexadecane–4-methylcylohexanone–*n*-hexane
VI. *n*-Tetradecane–*n*-hexane–2-bromobutane
VII. *n*-Tetradecane–4-methylcyclohexanone–*n*-hexane
VIII. *n*-Hexadecane–*n*-tetradecane–2-bromobutane
IX. *n*-Hexadecane–*n*-tetradecane–*n*-hexane
X. *n*-Hexadecane–*n*-tetradecane–4-methylcyclohexanone
XI. Carbon tetrachloride–*n*-hexane–benzene

The viscometric data include viscosity as a function of composition as volume and mole fraction, comparison of experimental viscosities with those calculated with several different equations, and excess Gibbs free energy of activation of flow. Volumetric data include density as a function of composition as volume and mole fraction and excess volumes of mixing.

Some properties of the ternary systems are related to those of the binary subsystems. Unless stated otherwise, it may be assumed that the pertinent information on the corresponding binary behavior has been reported (*8*).

Very little attention has previously been given to fitting viscosity behavior in ternary systems, so results by several alternative approaches are described in some detail. With the one system composed solely of *n*-alkanes, IX, the results are considered in terms of the congruence principle (*3*).

EXPERIMENTAL

Equipment. A thermostatically controlled bath constant to ±0.01° C. was used. Bath temperature was set and monitored with a Beckman thermometer which had been standardized against a certified thermometer. Times were measured with an electric stopclock calibrated against an electronic time standard. Weighings were made with a precision balance and certified balance weights. Density determination involved use of a cathetometer which indicated length to the nearest ±0.05 mm.

Three Cannon-Fenske viscometers of different capillary diameters were used because of the tenfold range of viscosities of the components. The viscometers were calibrated with National Bureau of Standards oils, and experimental results by the different viscometers were in agreement. Kinetic energy corrections were applied to viscosity data. Errors due to alignment and loading of viscometers were minimized by reproducible precautionary procedures.

Densities were determined with Lipkin pycnometers constructed with precision glass capillary tubing of 1-mm. i.d. Total pycnometer volume was 3 ml. Pycnometers were calibrated with distilled water, with heights of liquid in the capillary arms measured then, as in determining unknown densities later, relative to a single etched mark on each arm.

In making determinations, both pycnometers and viscometers were maintained in the bath until at least two consecutive measurements of the liquid height in the capillaries or the flow time indicated that the sample had reached the temperature of the bath. As the ambient temperature was not far below bath temperature, time required for the mixtures to reach bath temperature was short, and evaporation of mixtures from either pycnometers or viscometers was experimentally negligible for even the most volatile mixtures.

Liquids were mixed in a modified glass syringe sealed by glass at the needle end. Again evaporation rates were negligible. Mixtures were transferred to viscometers and pycnometers by overpressure through capillary tubing. The mixing syringe, transfer tubing, viscometers and pycnometers were all provided with ball-and-socket joints to minimize evaporation effects accompanying transfer. Joints were treated with low boiling solvent after sample transfer to remove traces of high boiling components on those surfaces.

Replication of experimental measurements has not been routinely followed. Uncertainties in a given property in Table I presumably should not be greater than those reported as typical for the binary subsystems (8): kinematic viscosity, ±0.10%; density, ±0.009%; excess volume, ±0.02 ml. per mole; excess Gibbs free energy of flow, ±0.7 cal. per mole.

Materials. As all components were liquid, routine fractional distillation techniques in a 48-inch Vigreux column were used for purification. Identification of the starting materials, a description of the specific procedures in purifying each component, and a tabulated comparison of the densities, viscosities, and refractive indices of the purified components with literature values have been given (8).

Table I. Properties of Ternary Mixtures at 25° C.

First-Named Component[a]		Second-Named Component[a]					
Volume fraction	Mole fraction	Volume fraction	Mole fraction	Kinematic Viscosity, Cs.	Density, G./Ml.	Δ^*G^E, Cal./Mole	ΔV^E, Ml./Mole
			n-Hexadecane–*n*-hexane–2-bromobutane				
0.7000	0.4873	0.1539	0.2393	1.6854	0.8233	196.3	0.07
0.5976	0.3755	0.1932	0.2712	1.3176	0.8492	194.4	0.07
0.5133	0.2961	0.1969	0.2359	1.1034	0.8873	186.6	0.14
0.5246	0.3115	0.2609	0.3461	1.1297	0.8438	188.1	0.09
0.4451	0.2462	0.2839	0.3508	0.9570	0.8683	169.9	0.11
0.3481	0.1712	0.1482	0.1628	0.7963	0.9553	141.1	0.24
0.3566	0.1839	0.3235	0.3727	0.7964	0.8876	137.2	0.05
0.3507	0.1875	0.4971	0.5936	0.7975	0.7873	142.0	−0.08
0.2710	0.1262	0.1846	0.1921	0.6855	1.0110	108.6	0.19
0.2752	0.1334	0.3518	0.3807	0.6822	0.9098	105.9	0.08
0.2673	0.1342	0.5383	0.6035	0.6784	0.8030	107.8	−0.19
0.1843	0.0796	0.1350	0.1302	0.5922	1.0827	74.9	0.16
0.1779	0.0794	0.3206	0.3194	0.5697	0.9752	60.5	0.11
0.1968	0.0922	0.4901	0.5131	0.5924	0.8652	73.9	0.04
0.1772	0.0849	0.6654	0.7122	0.5814	0.7701	72.2	−0.03
			n-Hexadecane–benzene–*n*-hexane				
0.7586	0.5315	0.1232	0.2836	1.9488	0.7681	183.0	0.45
0.5287	0.2957	0.1950	0.3586	1.1751	0.7575	165.8	0.29
0.5121	0.2691	0.2862	0.4941	1.1538	0.7738	154.7	0.62
0.3604	0.1850	0.1513	0.2552	0.8459	0.7293	122.7	0.11
0.3873	0.1873	0.2961	0.4706	0.9033	0.7621	107.9	0.47
0.3579	0.1557	0.4942	0.7030	0.9219	0.8000	98.2	0.75
0.1755	0.0798	0.1731	0.2586	0.6066	0.7122	35.3	0.20
0.1795	0.0757	0.3409	0.4724	0.6313	0.7478	10.6	0.42
0.1807	0.0707	0.5186	0.6666	0.6799	0.7859	11.6	0.50
0.1863	0.0686	0.6787	0.8205	0.7447	0.8212	29.5	0.49
0.6112	0.3605	0.2054	0.3979	1.3929	0.7685	178.6	0.50
0.4436	0.2238	0.2809	0.4657	1.0057	0.7653	132.0	0.48
0.2704	0.1281	0.2004	0.3120	0.7178	0.7292	73.0	0.18
0.2789	0.1221	0.3760	0.5406	0.7577	0.7665	56.0	0.50
0.2659	0.1074	0.5429	0.7202	0.7951	0.8007	55.7	0.56
			n-Hexadecane–carbon tetrachloride–benzene				
0.7192	0.4489	0.1515	0.2860	1.8520	0.9031	201.9	0.85
0.5178	0.2523	0.1886	0.2780	1.2339	0.9481	174.4	0.94
0.5293	0.2648	0.2956	0.4474	1.2731	1.0234	184.2	0.83
0.3668	0.1551	0.3204	0.4100	0.9627	1.0574	132.0	0.71
0.3500	0.1484	0.4878	0.6257	0.9424	1.1786	134.1	0.59
0.1777	0.0625	0.1366	0.1453	0.7765	0.9484	59.7	0.42
0.1864	0.0670	0.2980	0.3242	0.7583	1.0618	67.0	0.44
0.1914	0.0704	0.4924	0.5477	0.7467	1.1994	73.8	0.39
0.1930	0.0723	0.6747	0.7648	0.7445	1.3290	78.6	0.34
0.6116	0.3318	0.1716	0.2817	1.4637	0.9273	192.1	0.92
0.4520	0.2072	0.2743	0.3805	1.1100	1.0158	162.2	0.83
0.2766	0.1063	0.1928	0.2240	0.8610	0.9768	96.1	0.61
0.2712	0.1056	0.3705	0.4362	0.8373	1.1035	99.9	0.56
0.2689	0.1062	0.5334	0.6374	0.8263	1.2198	101.3	0.49
			n-Hexadecane–carbon tetrachloride–*n*-hexane				
0.6887	0.4597	0.1441	0.2910	1.7140	0.8682	198.9	0.10
0.5095	0.2886	0.2022	0.3465	1.1369	0.9017	172.4	0.03
0.5191	0.2868	0.2738	0.4576	1.1833	0.9681	174.2	0.24
0.3749	0.1999	0.1316	0.2122	0.8522	0.8218	139.2	−0.21
0.3668	0.1798	0.3274	0.4855	0.8583	1.0007	118.1	0.14
0.1885	0.0897	0.1267	0.1824	0.5979	0.7953	62.0	−0.11

[a] Refers to first and second components of individual ternary systems.

(Continued)

Table I. Properties of Ternary Mixtures at 25° C. (*Continued*)

First-Named Component[a]		Second-Named Component[a]					
Volume fraction	Mole fraction	Volume fraction	Mole fraction	Kinematic Viscosity, Cs.	Density, G./Ml.	Δ^*G^E, Cal./Mole	ΔV^E, Ml./Mole
n-Hexadecane–carbon tetrachloride–*n*-hexane (*Continued*)							
0.1904	0.0844	0.3232	0.4337	0.6019	0.9772	36.3	0.03
0.1898	0.0790	0.5081	0.6400	0.6307	1.1474	33.6	0.18
0,1929	0.0764	0.6677	0.8002	0.6898	1.2950	57.4	0.23
0.6298	0.3904	0.1976	0.3706	1.5127	0.9106	200.5	0.18
0.4449	0.2345	0.2682	0.4277	0.9964	0.9552	147.7	0.08
0.2740	0.1344	0.1814	0.2691	0.6966	0.8562	89.3	−0.15
0.2647	0.1201	0.3752	0.5150	0.7022	1.0334	69.3	0.12
0.2654	0.1137	0.5413	0.7014	0.7481	1.1863	77.8	0.25
n-Hexadecane–4-methylcyclohexanone–*n*-hexane							
0.7330	0.5434	0.1276	0.2260	2.2506	0.7730	118.7	−0.08
0.6228	0.4168	0.1872	0.2992	1.8716	0.7752	115.6	0.01
0.5727	0.3271	0.1845	0.2734	1.4788	0.7640	113.8	−0.12
0.5229	0.3206	0.2745	0.4019	1.6884	0.7861	90.7	0.01
0.4490	0.2610	0.2634	0.3656	1.4031	0.7752	86.7	−0.11
0.3533	0.1914	0.3113	0.4028	1.2266	0.7770	59.8	−0.22
0.3541	0.1890	0.4978	0.6346	1.6447	0.8232	41.0	0.15
0.2598	0.1338	0.1867	0.2296	0.8539	0.7347	55.9	−0.31
0.2731	0.1379	0.5396	0.6508	1.4830	0.8253	27.3	0.00
0.1860	0.0919	0.1325	0.1563	0.7032	0.7123	46.5	−0.32
0.1784	0.0864	0.3278	0.3793	0.8836	0.7616	4.9	−0.30
0.1783	0.0854	0.4790	0.5480	1.0853	0.8001	−11.5	−0.23
0.1926	0.0917	0.6778	0.7706	1.5366	0.8513	2.2	0.03
n-Tetradecane–*n*-hexane–2-bromobutane							
0.6943	0.5081	0.1434	0.2082	1.3458	0.8250	133.6	0.08
0.6280	0.4355	0.1834	0.2524	1.1896	0.8337	140.5	0.09
0.5072	0.3167	0.2041	0.2528	0.9476	0.8803	129.9	0.20
0.5283	0.3418	0.2702	0.3469	0.9868	0.8311	133.4	0.05
0.4325	0.2586	0.2857	0.3389	0.8278	0.8691	107.1	0.05
0.3658	0.2006	0.1401	0.1524	0.7518	0.9879	107.1	0.24
0.3530	0.1996	0.3196	0.3585	0.7229	0.8877	95.1	0.10
0.2806	0.1460	0.1899	0.1960	0.6466	1.0003	76.3	0.20
0.2823	0.1522	0.3504	0.3748	0.6430	0.9043	74.2	0.08
0.2792	0.1563	0.5291	0.5875	0.6464	0.7998	78.3	−0.09
0.1959	0.0953	0.1502	0.1450	0.5721	1.0659	53.1	0.16
0.1785	0.0889	0.3262	0.3222	0.5469	0.9700	40.1	0.07
0.1811	0.0935	0.4965	0.5088	0.5493	0.8670	42.3	0.04
0.1891	0.1018	0.6636	0.7088	0.5669	0.7639	53.4	−0.11
n-Tetradecane–4-methylcyclohexanone–*n*-hexane							
0.7059	0.5390	0.1473	0.2386	1.7276	0.7671	61.7	0.02
0.6274	0.4512	0.1754	0.2676	1.5371	0.7663	65.3	−0.03
0.5424	0.3679	0.1760	0.2532	1.2997	0.7582	68.4	−0.18
0.5358	0.3590	0.2589	0.3680	1.4532	0.7780	46.3	0.00
0.4473	0.2829	0.2728	0.3659	1.2579	0.7728	43.1	−0.11
0.3825	0.2355	0.1209	0.1579	0.9023	0.7279	68.9	−0.31
0.3644	0.2185	0.3095	0.3936	1.1312	0.7739	22.9	−0.19
0.3770	0.2247	0.4714	0.5961	1.4843	0.8153	7.3	0.10
0.2771	0.1596	0.1802	0.2203	0.8165	0.7323	32.0	−0.34
0.2869	0.1640	0.3479	0.4218	1.0472	0.7758	8.2	−0.22
0.2832	0.1594	0.5151	0.6152	1.3307	0.8175	−6.7	−0.06
0.2110	0.1176	0.1312	0.1552	0.6923	0.7124	27.1	−0.28
0.2093	0.1151	0.2918	0.3404	0.8421	0.7535	−6.4	−0.27
0.2136	0.1162	0.4742	0.5470	1.0975	0.8005	−21.1	−0.19
n-Hexadecane–*n*-tetradecane–2-bromobutane							
0.1403	0.0635	0.1551	0.0791	0.7053	1.1068	108.4	0.33
0.1861	0.0889	0.1796	0.0966	0.7971	1.0724	131.2	0.39
0.2056	0.1071	0.2693	0.1579	0.9606	1.0184	154.5	0.48
0.2781	0.1439	0.1831	0.1067	0.9566	1.0258	160.2	0.51
0.2891	0.1631	0.2739	0.1740	1.1541	0.9760	175.6	0.52
0.1614	0.0976	0.4872	0.3315	1.2941	0.9325	158.0	0.55
0.3416	0.2114	0.3172	0.2210	1.3900	0.9294	174.2	0.56
0.4930	0.3055	0.1551	0.1082	1.4230	0.9360	189.3	0.61
0.1875	0.1232	0.5437	0.4021	1.5441	0.8923	154.0	0.58
0.3555	0.2344	0.3657	0.2714	1.5860	0.8993	168.5	0.51
0.5321	0.3556	0.1879	0.1414	1.6708	0.9014	184.1	0.58
0.1644	0.1197	0.6640	0.5444	1.8887	0.8449	123.3	0.47
0.3167	0.2265	0.4835	0.3893	1.8744	0.8602	149.5	0.52
0.5025	0.3794	0.3299	0.2805	2.1242	0.8466	143.6	0.46
0.6801	0.5152	0.1407	0.1200	2.1866	0.8538	159.3	0.53

(*Continued on page 58*)

Table I. Properties of Ternary Mixtures at 25° C. (*Continued*)

First-Named Component[a]		Second-Named Component[a]					
Volume fraction	Mole fraction	Volume fraction	Mole fraction	Kinematic Viscosity, Cs.	Density, G./Ml.	Δ^*G^E, Cal./Mole	ΔV^E, Ml./Mole
n-Hexadecane–*n*-tetradecane–*n*-hexane							
0.1253	0.0650	0.1364	0.0796	0.6754	0.6857	105.3	−0.39
0.1857	0.1028	0.1795	0.1119	0.8105	0.6976	141.3	−0.49
0.1793	0.1046	0.2685	0.1763	0.9256	0.7064	154.1	−0.55
0.2612	0.1521	0.1756	0.1151	0.9323	0.7060	164.4	−0.53
0.2664	0.1650	0.2626	0.1831	1.0983	0.7158	176.0	−0.56
0.1337	0.0878	0.4935	0.3651	1.2574	0.7246	157.8	−0.56
0.3190	0.2118	0.3020	0.2258	1.3075	0.7259	175.3	−0.55
0.4884	0.3274	0.1255	0.0947	1.3548	0.7271	192.5	−0.61
0.1841	0.1297	0.5304	0.4208	1.5182	0.7340	153.9	−0.50
0.3663	0.2648	0.3593	0.2924	1.6384	0.7372	165.8	−0.54
0.5435	0.3995	0.1829	0.1514	1.7305	0.7389	179.5	−0.49
0.1480	0.1105	0.6421	0.5396	1.7614	0.7411	132.3	−0.40
0.3306	0.2522	0.4653	0.3998	1.8828	0.7436	141.6	−0.40
0.4873	0.3777	0.3089	0.2696	1.9790	0.7453	151.7	−0.40
0.6570	0.5182	0.1400	0.1243	2.0912	0.7472	161.8	−0.42
n-Hexadecane–*n*-tetradecane–4-methylcyclohexanone							
0.6376	0.5022	0.1850	0.1640	2.9264	0.7916	42.6	0.67
0.5358	0.3808	0.1883	0.1507	2.6552	0.8056	50.9	0.56
0.5378	0.4167	0.2783	0.2428	2.8169	0.7915	39.7	0.67
0.4496	0.3187	0.2800	0.2235	2.6100	0.8036	50.0	0.63
0.3704	0.2188	0.1441	0.0959	2.2875	0.8348	52.5	0.62
0.3689	0.2503	0.3190	0.2438	2.4802	0.8088	47.1	0.67
0.3720	0.3010	0.5038	0.4590	2.7645	0.7815	20.6	0.46
0.2679	0.1506	0.1878	0.1188	2.1705	0.8427	44.6	0.59
0.2797	0.1832	0.3745	0.2761	2.3680	0.8130	42.3	0.64
0.2720	0.2044	0.5387	0.4558	2.5691	0.7900	28.4	0.54
0.1846	0.0953	0.1543	0.0897	2.0260	0.8600	31.9	0.45
0.2021	0.1180	0.3130	0.2057	2.2027	0.8333	46.4	0.55
0.1760	0.1177	0.5136	0.3866	2.3281	0.8067	32.6	0.61
0.1863	0.1460	0.6763	0.5968	2.5810	0.7817	17.5	0.41
Carbon tetrachloride–*n*-hexane–benzene							
0.6962	0.7166	0.1572	0.1195	0.5157	1.3320	−38.4	0.14
0.5189	0.5342	0.2014	0.1531	0.5092	1.1958	−50.8	0.21
0.5384	0.5718	0.2819	0.2210	0.4828	1.1916	−63.3	0.25
0.3560	0.3570	0.1671	0.1237	0.5379	1.0876	−45.2	0.22
0.3619	0.3833	0.3181	0.2487	0.4875	1.0882	−70.2	0.29
0.3666	0.4172	0.5057	0.4249	0.4428	1.0214	−81.5	0.24
0.1844	0.1919	0.3142	0.2414	0.5110	0.9328	−73.9	0.34
0.1771	0.1976	0.5018	0.4133	0.4668	0.8870	−84.6	0.35
0.2141	0.2544	0.6503	0.5706	0.4400	0.8816	−72.0	0.27
0.6115	0.6331	0.1939	0.1482	0.5098	1.2628	−43.5	0.23
0.4452	0.4643	0.2552	0.1965	0.4979	1.1319	−60.7	0.20
0.2810	0.3215	0.5396	0.4557	0.4477	0.9530	−79.5	0.28
0.2932	0.3071	0.3050	0.2359	0.4999	1.0128	−68.9	0.25
0.2416	0.2415	0.1858	0.1371	0.5458	1.0025	−51.3	0.21

RESULTS

The experimental kinematic viscosities and densities of the mixtures are listed in Table I, as well as the excess molar volumes (ΔV^E) and the excess molar Gibbs free energies of activation of flow (Δ^*G^E). The excess molar volume is defined as

$$\Delta V^E = V - \sum_{i=1}^{n} X_i V_i$$

The excess molar Gibbs free energy of activation of flow is defined (*8*) through the Eyring viscosity equation (*5*):

$$\nu = \left(\frac{\lambda}{a}\right)^2 \frac{hN}{M} \exp\left(\Delta^*G/RT\right) \tag{1}$$

as

$$\Delta^*G^E = RT[\ln \eta V - \sum_{i=1}^{n} X_i \ln \eta_i V_i] \tag{2}$$

Thus if $\Delta^*G^E > 0$, the viscosity is greater than that of an ideal mixture. Ideal viscosity, Δ^*G^I, is defined by

$$\Delta^*G^I = \sum_{i=1}^{n} X_i \Delta^*G_i \tag{3}$$

For fitting of mixture viscosities, two recent equations combining an interaction model with empirical interaction parameters are available. That of Katti and Chaudhri (*10*), based upon the *s*-regular solution two-body model (*6*), may be expressed as (*7*)

$$\log \nu = \sum_{i=1}^{n} X_i \log \nu_i + \sum_{i=1}^{n} X_i \log M_i - \log \sum_{i=1}^{n} X_i M_i + \delta_{i\ldots n} \tag{4}$$

where

$$\delta_{i\ldots n} = 1/2 \sum_{i=1}^{n} \sum_{j=1}^{n} X_i X_j A_{ij} \tag{5}$$

Equation 4 has also been modified (*7*) by replacing the constant A_{ij} in Equation 5 by a power series in concentration

$$\delta_{i\ldots n} = \sum_{\substack{i=1 \\ i<j}}^{n} X_i X_j [A_{ij} + B_{ij}(X_i - X_j) + C_{ij}(X_i - X_j)^2 + \ldots] \qquad (6)$$

Heric and Brewer found (*8*) that in the binary subsystems, Equation 5 was in significantly greater error than Equation 6. Accordingly, only the latter has been considered here. The ternary results show, however, that an assumption of only binary interaction terms leads to a relatively large error. Thus for ternary systems, Equation 6 has been expanded to

$$\delta_{123} = \sum_{\substack{i=1 \\ i<j}}^{3} X_i X_j [A_{ij} + B_{ij}(X_i - X_j) + C_{ij}(X_i - X_j)^2 + \ldots] + X_1 X_2 X_3 [A_{123} + B_{123} X_1 + C_{123} X_2] \qquad (7)$$

Results by Equations 4 and 7 and the ternary constants of Equation 7 are given in Table II. The fitting of data here, as throughout this work, was done with the aid of a digital computer. Data have been weighted in fitting, also, throughout this work (*7*).

As the approach of Equation 6 is largely empirical, an alternative power expansion has also been considered. Thus instead of Equation 6 one may assume that

$$\delta_{i\ldots n} = \sum_{\substack{i=1 \\ i<j}}^{n} X_i X_j [A'_{ij} + B'_{ij} X_i + C'_{ij} X_i^2 + \ldots] \qquad (8)$$

so that in place of Equation 7 for the ternary systems,

$$\delta_{123} = \sum_{\substack{i=1 \\ i<j}}^{n} X_i X_j [A'_{ij} + B'_{ij} X_i + C'_{ij} X_i^2 + \ldots] + X_1 X_2 X_3 [A'_{123} + B'_{123} X_1 + C'_{123} X_2] \qquad (9)$$

In referring to these two different power series forms, the unprimed constants of Equation 7 are called symmetric because the series reduces to a single term in A_{ij} at $X_i = X_j = 0.5$. The other series, with primed constants, Equation 9, is called asymmetric.

Results by Equations 4 and 9 and the ternary constants of the latter are included in Table II. Binary asymmetric constants of Equation 8 (as well as asymmetric binary constants elsewhere below) were not reported previously. They are also omitted here, because they may be obtained by straightforward calculation from the available symmetric binary constants (*8*).

Another approach to viscosity correlation in ternary systems has been given by Kalidas and Laddha (*9*) as an extension of the three-body model McAllister applied to binary systems (*12*):

Table II. Mixture Viscosities by Equations 4 and 7 and 4 and 9

	Equations 4 and 7					Equations 4 and 9				
	Ternary Constants of Equation 7[a]			Error, %, as ν		Ternary Constants of Equation 9[a]			Error, %, as ν	
	A_{123}	B_{123}	C_{123}	Stand.[b]	Max.	A'_{123}	B'_{123}	C'_{123}	Stand.[b]	Max.
n-Hexadecane–*n*-hexane–2-bromobutane	2.8502			2.16	4.03	0.0436			0.34	0.80
n-Hexadecane–benzene–*n*-hexane	4.5739	−8.0366	2.5974	1.26	2.42	0.5996	−1.8061	1.7795	0.38	0.72
n-Hexadecane–carbon tetrachloride–benzene	1.7549	−2.8303	1.6498	0.66	1.08	−0.7288	1.2065	−0.0569	0.34	0.83
n-Hexadecane–carbon tetrachloride–*n*-hexane	3.9277	−7.9772	3.8289	1.73	2.73	−0.3638	−0.0618	1.8358	0.50	0.81
n-Hexadecane–4-methylcyclohexanone–*n*-hexane	4.0377	−4.9913	−1.3749	0.95	1.48	0.5424	−1.1294	0.4440	0.50	1.07
n-Tetradecane–*n*-hexane–2-bromobutane	1.6599			1.10	2.12	0.0721			0.31	0.93
n-Tetradecane–4-methylcyclohexanone–*n*-hexane	2.3617	−2.3705	−1.0388	0.26	0.53	0.2482	−0.5701	0.7828	0.28	0.67
n-Hexadecane–*n*-tetradecane–2-bromobutane	9.9509	−15.9025	−16.5659	2.40	4.46	−2.5934	1.5546	1.2924	0.36	0.89
n-Hexadecane–*n*-tetradecane–*n*-hexane	7.5846	−12.4683	−11.9923	1.59	3.61	−3.0985	2.5267	2.5111	0.30	0.82
n-Hexadecane–*n*-tetradecane–4-methylcyclohexanone	2.1745	−2.6251	−3.0989	0.45	0.88	0.7813	−2.1306	−1.6390	0.40	1.14
Carbon tetrachloride–*n*-hexane–benzene	−0.5447			1.01	1.78	−0.4024			0.31	0.62

[a] Component 1 is first- and component 2 is second-named of system.

[b] $\left\{\sum\left[\frac{100\,(\text{viscosity exptl.} - \text{viscosity calcd.})}{\text{viscosity exptl.}}\right]^2 / \text{number of observations}\right\}^{1/2}$

$$\log \nu = \sum_{i=1}^{n} X_i^3 \log \nu_i + \sum_{i=1}^{n} X_i^3 \log M_i - \log \sum_{i=1}^{n} X_i M_i +$$

$$3 \sum_{\substack{i=1 \\ i \neq j}}^{n} \sum_{j=1}^{n} X_i^2 X_j \log \left(\frac{2 M_i + M_j}{3} \right) +$$

$$\sum_{\substack{i=1 \\ i \neq j \neq k \neq i}}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} X_i X_j X_k \log \left(\frac{M_i + M_j + M_k}{3} \right) + \delta_{i \ldots n} \quad (10)$$

where

$$\delta_{i \ldots n} = 3 \sum_{\substack{i=1 \\ i \neq j}}^{n} \sum_{j=1}^{n} X_i^2 X_j \log \nu_{ij} + \sum_{\substack{i=1 \\ i \neq j \neq k \neq i}}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} X_i X_j X_k \log \nu_{ijk} \quad (11)$$

with ν_{ijk} independent of the order of i, j, and k. Both the two- and three-body models are based upon the Eyring absolute rate theory, Equation 1. The results by Equations 10 and 11 and ν_{ijk} values are given in Table III.

The viscosity data may also be fitted empirically without any theoretical basis in a form

$$\nu = \sum_{i=1}^{n} X_i \nu_i + \delta_{i \ldots n} \quad (12)$$

where $\delta_{i \ldots n}$ for a binary system is precisely of the symmetric form of Equation 6 and, for a ternary system, of Equation 7. In the study of the binary subsystems, Heric and Brewer found (*8*) that fitting the data with the power series of Equation 12 and 6 was practically equivalent in error to fitting with the more mathematically complex Equations 4 and 6. In the ternary systems, however, the former are clearly ineffective by comparison and are omitted.

For the excess Gibbs free energy of mixing, ΔG^E, in s-regular binary mixtures (*6*)

$$\Delta G^E = X_1 X_2 W_{12} \quad (13)$$

where W_{12} is an interaction parameter. In multicomponent s-regular mixtures,

$$\Delta G^E = \sum_{\substack{i=1 \\ i<j}}^{n} \sum_{j=1}^{n} X_i X_j W_{ij} \quad (14)$$

For the excess Gibbs free energy of activation of flow, $\Delta^* G^E$, a parallel concept (cf. Equation 5) yields, corresponding to Equation 13,

$$\Delta^* G^E = X_1 X_2 A_{12} \quad (15)$$

and, corresponding to Equation 14

$$\Delta^* G^E = \sum_{\substack{i=1 \\ i<j}}^{n} \sum_{j=1}^{n} X_i X_j A_{ij} \quad (16)$$

$\Delta^* G^E$ in some of the present binary subsystems is satisfied by the form of Equation 15, but, as Table IV shows, most require an expanded version of that equation:

$$\Delta^* G^E = X_1 X_2 [A_{12} + B_{12}(X_1 - X_2) + C_{12}(X_1 - X_2)^2 + \ldots] \quad (17)$$

Extension of Equation 16 to the 11 ternary systems, replacing each A_{ij} by an expansion of the form in Equation 17, represented $\Delta^* G^E$ rather poorly in all the systems. Thus for the ternary systems, it has been assumed that (cf. Equation 7)

$$\Delta^* G^E = \sum_{\substack{i=1 \\ i<j}}^{3} X_i X_j [A'_{ij} + B'_{ij} X_i + C'_{ij} X_i^2 + \ldots] + X_1 X_2 X_3 A'_{123} \quad (18)$$

The error by Equation 18 and the asymmetric ternary constants are given in Table V. The adoption of a single

Table III. Mixture Viscosities by Equations 10 and 11

	ν_{ijk}	Error, %, as ν	
		Stand.[a]	Max.
n-Hexadecane–n-hexane–2-bromobutane	1.6549	0.81	2.00
n-Hexadecane–benzene–n-hexane	1.9980	1.33	3.21
n-Hexadecane–carbon tetrachloride–benzene	1.8781	0.32	0.72
n-Hexadecane–carbon tetrachloride–n-hexane	1.9101	1.15	2.28
n-Hexadecane–4-methylcyclohexanone–n-hexane	2.0494	0.85	1.67
n-Tetradecane–n-hexane–2-bromobutane	1.1856	0.38	0.96
n-Tetradecane–4-methylcyclohexanone–n-hexane	1.5111	0.57	1.15
n-Hexadecane–n-tetradecane–2-bromobutane	2.1633	0.54	1.01
n-Hexadecane–n-tetradecane–n-hexane	2.0459	0.43	0.96
n-Hexadecane–n-tetradecane–4-methylcyclohexanone	2.8156	0.54	1.50
Carbon tetrachloride–n-hexane–benzene	0.4139	0.31	0.53

[a] Defined in Table II.

Table IV. Excess Gibbs Free Energy of Activation of Flow, Binary Subsystems

	Binary Constants, Equation 17[a]				Error, Cal. per Mole	
	A_{12}	B_{12}	C_{12}	D_{12}	Stand.[b]	Max.
n-Hexadecane–n-hexane	820.8	−273.3	129.0	55.5	1.2	2.7
n-Hexadecane–2-bromobutane	794.1	−335.9	138.7	81.1	1.5	2.9
n-Hexadecane–carbon tetrachloride	841.7	−281.3	122.9	−103.3	0.6	1.2
n-Hexadecane–benzene	774.4	−227.1	73.7	77.0	0.8	1.3
4-Methylcyclohexanone–n-hexadecane	267.7	155.9	−48.2	−74.2	0.9	2.2
n-Tetradecane–n-hexane	578.5	−176.8	26.5		2.6	5.6
n-Tetradecane–2-bromobutane	563.6	−186.5	47.3		0.4	0.9
4-Methylcyclohexanone–n-tetradecane	77.9	32.3	−60.0		0.5	1.0
2-Bromobutane–n-hexane	−104.7				0.6	1.3
Carbon tetrachloride–n-hexane	−285.0	−105.5	−52.8		0.5	1.0
Benzene–n-hexane	−353.2	−134.5	−71.0		0.7	1.2
4-Methylcyclohexanone–n-hexane	−331.4	−32.1	−63.1		0.5	0.7
Carbon tetrachloride–benzene	26.6				0.7	1.5
n-Hexadecane–n-tetradecane	8.0	−4.0	−49.6	−94.1	1.8	4.8

[a] Component 1 is first named of pair. [b] Defined in Table II.

Table V. Excess Gibbs Free Energy of Activation of Flow and Excess Volume, Ternary Systems

	Free Energy			Volume		
	Ternary Constant A'_{123} Eq. 18	Error, Cal. per Mole		Ternary Constant A'_{123} Eq. 20	Error, Ml. per Mole	
		Stand.[a]	Max.		Stand.[a]	Max.
n-Hexadecane–*n*-hexane–2-bromobutane	50	2.5	6.1	−0.42	0.04	0.09
n-Hexadecane–benzene–*n*-hexane	692	6.9	13.8	−0.45	0.01	0.01
n-Hexadecane–carbon tetrachloride–benzene	−325	2.9	5.9	−1.11	0.01	0.02
n-Hexadecane–carbon tetrachloride–*n*-hexane	246	3.0	6.0	−4.36	0.06	0.13
n-Hexadecane–4-methylcyclohexanone–*n*-hexane	306	5.5	10.4	1.14	0.04	0.12
n-Tetradecane–*n*-hexane–2-bromobutane	42	1.9	5.5	0.11	0.03	0.06
n-Tetradecane–4-methylcyclohexanone–*n*-hexane	226	3.0	5.8	2.51	0.03	0.04
n-Hexadecane–*n*-tetradecane–2-bromobutane	−1143	4.0	7.8	−0.57	0.03	0.07
n-Hexadecane–*n*-tetradecane–*n*-hexane	−1129	4.6	9.0	4.59	0.02	0.05
n-Hexadecane–*n*-tetradecane–4-methylcyclohexanone	−95	5.2	10.8	−0.51	0.05	0.14
Carbon tetrachloride–*n*-hexane–benzene	−239	1.9	3.7	1.09	0.04	0.07

[a] Defined in Table II.

constant for the ternary terms in Equation 18 was an arbitrary choice. Higher ternary terms were not considered.

Coursey and Heric (*3*) found that viscosity in some *n*-alkane mixtures may be treated by the congruence principle of Brønsted and Koefoed (*2*). The hexadecane-tetradecane-hexane system has been treated here relative to the hexadecane-hexane binary in the manner previously described (*3*). Index numbers of the ternary mixtures and errors in both Δ^*G^E and ν by this method of prediction are given in Table VI.

Interpretation of volumetric behavior is not a prime purpose of the present work and these data are not of high precision. Density data have been routinely taken, however, to relate kinematic and dynamic viscosities and to extend the broad comparison of volumetric and viscometric behavior noted in the binary subsystems (*8*). With sufficient data in hand it was thought worthwhile to report fitting of the excess volumes to concentration as an addition to the literature of this phenomenon. For the binary subsystems, the equation used by Rastogi *et al.* (*13*) has been used. Its form resembles several equations above:

$$\Delta V^E = X_1X_2[A_{12} + B_{12}(X_1 - X_2) + C_{12}(X_1 - X_2)^2 + \ldots] \qquad (19)$$

The symmetric constants of Equation 19 and the errors thereby are listed in Table VII.

For the ternary systems, a summation of binary terms of the form of Equation 19 was found to be in excessive error. Accordingly, ternary systems have been fitted to the form

$$\Delta V^E = \sum_{\substack{i=1 \\ i<j}}^{n} X_iX_j[A'_{ij} + B'_{ij}X_i + C'_{ij}X_i^2 + \ldots] + X_1X_2X_3A'_{123} \qquad (20)$$

Table V shows the results by Equation 20 and the ternary asymmetric constants. As with Δ^*G^E ternary constants, only one ternary ΔV^E constant was considered in Equation 20.

Table VI. Application of Congruence Principle to System Hexadecane–Tetradecane–Hexane[a]

Index No.	Δ^*G^E Error,[b] Cal./Mole	ν Error, Cs.	ν Error, %[c]
7.287	−6.1	−0.007	1.0
7.924	−4.8	−0.007	0.8
8.456	−8.5	−0.013	1.4
8.442	−4.6	−0.008	0.8
9.115	−5.4	−0.010	0.9
9.799	−12.4	−0.027	2.1
9.925	−11.1	−0.024	1.9
10.031	−8.7	−0.020	1.5
10.664	−8.5	−0.021	1.4
10.987	−7.3	−0.020	1.2
11.206	−5.9	−0.018	1.0
11.421	−6.3	−0.020	1.1
11.721	−6.4	−0.021	1.1
11.934	−5.8	−0.020	1.0
12.176	−5.9	−0.021	1.0

[a] Data points presented in same sequence used for this system in Table I. [b] Error = exptl. value − calcd. value. [c] Standard deviation (defined in Table II) 1.3%.

DISCUSSION

Components for these viscosity studies were chosen with the intent of considering mixtures with molecules of significantly different size and flow behavior. The seven components may be put into two groups—tetradecane and hexadecane, with molar volumes greater than 260 ml. per mole, and the others, with molar volumes of 130 ml. per mole or less. This difference is essentially paralleled by their kinematic viscosities, except for that of 4-methylcyclohexanone, which falls between the two groups. A pattern of the study may be established as follows: systems of one large and two small molecular types, I through VII; systems of two large and one small molecular type, VIII through X; and a system of small molecular type only, XI. The large molecule is hexadecane in systems I through V, and tetradecane in systems VI and VII.

In terms of behavior encountered in the binary subsystems (*8*), the ternary systems contain both types in which the three subsystems depart from ideality in the same algebraic sense, and in which one of the three pairs differs in sign from the other two. The several examples of sign variation within the properties of a system in Table I reflect this.

Table VII. Excess Volume, Binary Subsystems

	Binary Constants, Equation 19[a]				Error, Ml. per Mole	
	A_{12}	B_{12}	C_{12}	D_{12}	Stand.[b]	Max.
n-Hexadecane–*n*-hexane	−2.30	0.99			0.03	0.06
n-Hexadecane–2-bromobutane	2.12	−0.62	0.59		0.02	0.03
n-Hexadecane–carbon tetrachloride	2.46	−1.58	0.66		0.03	0.07
n-Hexadecane–benzene	4.19	−2.62	1.57		0.03	0.05
4-Methylcyclohexanone–*n*-hexadecane	2.90	0.48			0.02	0.03
n-Tetradecane–*n*-hexane	−2.09	0.42	−1.09		0.01	0.02
n-Tetradecane–2-bromobutane	1.92	−0.42	0.39		0.02	0.03
4-Methylcyclohexanone–*n*-tetradecane	2.34	0.11			0.03	0.04
2-Bromobutane–*n*-hexane	0.52	−0.42			0.02	0.05
Carbon tetrachloride–*n*-hexane	0.62				0.03	0.06
Benzene–*n*-hexane	1.75				0.02	0.03
4-Methylcyclohexanone–*n*-hexane	−1.57	−0.53			0.02	0.03
Carbon tetrachloride–benzene	0.20				0.03	0.05
n-Hexadecane–*n*-tetradecane	0.26	0.48	0.25	1.35	0.03	0.06

[a] Component 1 is first-named of pair. [b] Defined in Table II.

The results by the modified equation of Katti and Chaudhri considered in Table II show that the asymmetric form of the deviation function of Equation 9 is clearly an improvement over the symmetric form of Equation 7. The standard error with the asymmetric constants ranges from 0.3 to 0.5% in the kinematic viscosity, compared with 0.3 to 2.4% with the symmetric constants.

In establishing this error comparison, the same number of constants has been used by both approaches in a given system. In selecting the number of constants for each system, all orders of power expansion through the sixth, including cross terms in concentrations, were examined. That order was selected for a system beyond which convergence to lesser error became relatively slow compared with the previous terms. Thus the order of the fitting equations varies between systems. (A like procedure has been followed below in other fitting equations.) Only three of the 11 systems (I, VI, and XI) require but one ternary fitting constant. The first two involve both hexane and 2-bromobutane as a common pair. The kinematic viscosities of this pair differ by less than 1%. The third system is the only one involving three small molecular components.

Equations 10 and 11 of Kalidas and Laddha require only seven constants in a ternary system (six binary constants and one ternary constant), while the method of Table II requires from 9 to 12 constants for the present systems. Tables II and III allow a comparison between the errors of the two approaches. Whereas both approaches give comparable errors for seven systems, the errors in systems I, II, IV, and V by the Kalidas-Laddha equation are significantly larger. Each of these four systems contains the hexadecane-hexane pair, plus a third component of small size. The behavior of this pair as a binary system, however, has not been found unusual, compared with the others (*8*). The behavior is apparently due to an effect in the Kalidas-Laddha equation itself. There is a tendency in these four ternary systems for calculated values to be systematically high at the higher hexadecane concentrations. For systems VI and VII, differing from I and V by the substitution of tetradecane for hexadecane, the error by the Kalidas-Laddha approach is rather less than in I and V. There is no parallel between the number of ternary constants required for best fitting of a system by Equations 4 and 9 and the errors in Equations 10 and 11.

Redlich and Kister (*14*) have suggested fitting equations for the excess free energy of mixing that are of the form of Equation 17, and for this reason Equation 17 has been considered here for fitting Δ^*G^E. Table IV shows that about half of the binary subsystems require four terms to represent Δ^*G^E to within 1 to 2 cal. per mole. Only two systems, 2-bromobutane–hexane and benzene–carbon tetrachloride, are sufficiently simple that a single constant represents the behavior. Δ^*G^E is relatively small in both of these systems.

Table V shows that Equation 18 is moderately useful in representing Δ^*G^E in the ternary systems, with the poorest fit about ten times the experimental reproducibility of Δ^*G^E. There is little correlation between the error in fitting Δ^*G^E by Equation 18 and the nature of the component pairs.

Application of the congruence principle to viscosity in *n*-alkane mixtures has been described (*3*). The method allows a prediction of mixture viscosities, rather than providing a means for fitting measured mixture viscosities. Results by applying the congruence principle to the only system of the study which can be treated in this manner—i.e., IX—show in Table VI a significant agreement between experimental and predicted values, although the error is systematically of the same sign. The standard error for 15 mixtures of index numbers (average carbon chain length in the mixture) ranging from 7 to 12 is 1.3% in kinematic viscosity. Over this concentration range the viscosity varies from 0.7 to 2.1 centistokes and Δ^*G^E reaches a maximum of over 190 cal. per mole. The error in Δ^*G^E ranges from 5 to 12 cal. per mole, with the greatest error at the maximum Δ^*G^E of the system. The percentage error in viscosity remains relatively constant for all points and is only two to three times that of applying the fitting equations of Tables II and III to this system.

It is of interest to compare results by the congruence principle with those in applying some other equations for predicting mixture viscosities. As for an ideal mixture Δ^*G^E is zero, so by Equation 2 the ideal viscosity is given by

$$\ln \eta V = \sum_{i=1}^{n} X_i \ln \eta_i V_i$$

Other equations for the prediction of viscosity in mixtures include those employed by Bingham (*1*),

$$\Phi = \sum_{i=1}^{n} X_i \Phi_i$$

Kendall and Monroe (*11*)

$$\ln \eta = \sum_{i=1}^{n} X_i \ln \eta_i$$

and Cronauer *et al.* (*4*),

$$\ln \nu = \sum_{i=1}^{n} X_i \ln \nu_i$$

By these last four equations, the standard errors in system IX are 23.1, 46.9, 18.4, and 15.8%, respectively. The sign of the error in each instance is the same as that found in Table VI. The improvement through the use of the congruence principle is pronounced.

In fitting the excess volumes of the binary subsystems (Table VII), it is generally necessary to have more than one constant, except for some of the systems of small molecular components. All binary subsystems have excess volume of the same sign in a given system except for tetradecane-hexadecane, which shows a sign inversion (*8*). In the ternary systems, the excess volumes (Table V) are fitted as well with one ternary constant as the binary subsystems are fitted. In contrast, for the free energy (Tables IV and V) the errors in the binary subsystems are smaller than those in the ternary systems.

Mere comparison of the algebraic signs of the excess volumes and the excess Gibbs free energies of activation of flow in the ternary systems (Table I) is sufficient to establish the general lack of correlation between these two properties here. The behavior is consistent with that which would be projected from the results of the binary subsystems (*8*). Only two of the ternary systems (IX and XI) behave normally relative to the common assumption that ΔV^E and $\Delta^* G^E$ tend toward opposite sign as a consequence of the major role of free volume effects on viscosity behavior. The first of these two systems contains only small molecules, and thus resembles more the type of system upon which the assumption of the large influence of free volume on viscosity has commonly been based. The second system contains *n*-alkanes only, and the behavior is essentially the resultant of hexane-hexadecane and hexane-tetradecane interactions. Both the excess volumetric and excess viscometric effects are small for the tetradecane-hexadecane pair. Other viscometric factors are clearly of considerable importance in most of the systems. Segmented flow in the large molecules, for example, clearly involves the probability of significant entropy effects.

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NOMENCLATURE

A, B, C, D = symmetric constants for fitting of data
A', B', C', D' = asymmetric constants for fitting of data
$\Delta^* G$ = molar Gibbs free energy of activation of flow, cal./mole
$\Delta^* G_i$ = molar Gibbs free energy of activation of flow for *i*th mixture component in its pure state, cal./mole
M = molecular weight
N = Avogadro number
R = gas constant, cal./deg. mole
T = absolute temperature, ° K.
V = molar volume, ml./mole
ΔV = molar volume of mixing, ml./mole
W = interaction parameter, cal./mole
X = mole fraction
a = distance through which shearing force acts, cm.
h = Planck constant, erg sec.
η = dynamic viscosity, poises
λ = distance between adjacent moving layers of molecules, cm.
ν = kinematic viscosity—i.e., dynamic viscosity/density, stokes
ν_{ij}, ν_{ijk} = constants of Equations 10 and 11
Φ = fluidity—i.e., 1/dynamic viscosity, poise^{-1}

Subscript letters or numbers indicate component(s) associated with given property or symbol.

Superscripts

E = excess
i = ideal

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High Temperature Heat Contents of Lead Silicates

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High temperature heat contents of tetralead silicate, lead orthosilicate, and lead metasilicate were determined from room temperature to just below the melting points. Total or partial glass formation precluded heat of fusion determinations for these compounds. The results have been summarized in a table giving heat content values and by algebraic equations.

MOST PROPERTIES of the lead silicate system have been measured (*1, 3, 7, 8*). It is the purpose of this paper to supply the thermal data which are necessary for many thermodynamic calculations.

Three compounds have been identified in the lead silicate system: $4PbO \cdot SiO_2$, $2PbO \cdot SiO_2$, and $PbO \cdot SiO_2$ (*3*). The first of these, tetralead silicate, melts incongruently at 725° C. and occurs in three crystalline forms. The α form is stable above 720° C., the β form is stable between 155° and 720° C., and the γ form is stable below 120° C. Lead orthosilicate, $2PbO \cdot SiO_2$, melts incongruently at 743° C., and lead metasilicate, $PbO \cdot SiO_2$, melts congruently at 764° C.