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

LITERATURE CITED

(1) Bingham, E.C., "Fluidity and Plasticity," McGraw-Hill, New York, 1922.
(2) Brønsted, J.N., Koefoed, J., *Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd.* **22**, No. 17 (1946).
(3) Coursey, B.M., Heric, E.L., *Mol. Phys.* **13**, 287 (1967).
(4) Cronauer, D.C., Rothfus, R.R., Kermode, R.I., J. CHEM. ENG. DATA **10**, 131 (1965).
(5) Glasstone, S., Laidler, K.J., Eyring, H., "The Theory of Rate Processes," McGraw-Hill, New York, 1941.
(6) Guggenheim, E.A., "Mixtures," Oxford University Press, London, 1952.
(7) Heric, E.L., J. CHEM. ENG. DATA **11**, 66 (1965).
(8) Heric, E.L., Brewer, J.G., *Ibid.*, **12**, 576 (1967).
(9) Kalidas, R., Laddha, G.S., *Ibid.*, **9**, 142 (1964).
(10) Katti, P.K., Chaudhri, M.M., *Ibid.*, **9**, 442 (1964).
(11) Kendall, J., Monroe, K.P., *J. Am. Chem. Soc.* **39**, 1787 (1917).
(12) McAllister, R.A., *A.I.Ch.E.J.* **6**, 427 (1960).
(13) Rastogi, R.P., Nath, J., Misra, J., *J. Phys. Chem.* **71**, 2524 (1967).
(14) Redlich, O., Kister, A.T., *Ind. Eng. Chem.* **40**, 345 (1948).

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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.

Table I. Heat Content of Lead Silicates

T, ° K.	$H_T - H_{298.15}$, Cal./Mole	T, ° K.	$H_T - H_{298.15}$, Cal./Mole
	$PbO \cdot SiO_2$ (Crystal)		
387	2,260	666	9,640
444	3,750	719	11,150
520	5,490	740	12,250
572	7,070	757	12,710
572	7,090	817	14,010
620	8,410	840	14,870
626	8,550	882	15,720
658	9,540	904	16,410
	$PbO \cdot SiO_2$ (Glass)		
387	2,250	441	3,560
433	3,450	508	6,000
	$2PbO \cdot SiO_2$ (Crystal)		
388	3,490	765	19,130
444	5,330	817	20,860
521	8,290	833	20,780
572	10,590	882	23,740
626	12,720	904	24,210
668	14,630	941	26,180
719	17,110	966	27,760
740	17,860		
	$2PbO \cdot SiO_2$ (Glass)		
388	3,000	510	8,170
433	4,790	622	13,010
	$4PbO \cdot SiO_2$ (Crystal)		
444	9,550	835	35,350
521	13,710	841	36,550
573	17,330	882	40,300
626	20,930	904	41,200
665	24,380	941	45,010
754	30,780	967	45,850
816	34,640		

Table II. Constants in Equations 1 and 2

Material	a	$b \times 10^3$	$c \times 10^{-5}$	$-d \times 10^{-3}$
$PbO \cdot SiO_2$ (crystal)	38.064	−4.852	13.906	15.497
$PbO \cdot SiO_2$ (glass)	35.070	0.99	10.432	14.263
$2PbO \cdot SiO_2$ (crystal)	42.513	0.851	7.925	15.377
$2PbO \cdot SiO_2$ (glass)	37.810	7.66	8.061	14.776
$4PbO \cdot SiO_2$ (crystal)	45.300	16.9	−6.242	12.893

EXPERIMENTAL

Preparation. The three lead silicate compounds were prepared by melting the appropriate amounts of pure SiO_2 and PbO in a platinum crucible at 1000° C. When solution was complete, the resulting silicate was quenched rapidly; a glass was formed in the case of $2PbO \cdot SiO_2$ and $PbO \cdot SiO_2$.

The x-ray diffraction patterns for these materials were characteristic of amorphous materials. Quenched $4PbO \cdot SiO_2$ was partially or totally crystalline, so that no thermal data could be obtained for the glassy form. The $PbO \cdot SiO_2$ and $PbO \cdot SiO_2$ materials began to crystallize above 300° C., so that no thermal data for their glassy form could be obtained above this temperature.

The totally crystalline form of the three compounds was obtained by holding the materials at about 50° C. below their melting points for 48 hours. Well-defined x-ray diffraction patterns were thus obtained.

Measurements. Heat content measurements were conducted with a drop calorimeter for which the apparatus and procedure for calibration and measurement have been described (*2*, *9*). Sealed silica glass cells were used to contain the samples for measurements at lower temperatures. The heat content of silica glass was within 1% of the currently accepted value (*4*). At higher temperatures, platinum-lined silica cells were used. All heat content data have been corrected for the heat effect of the empty cells.

The method of Kubaschewski and Evans (*5*) was used for calibration. Six measurements in the temperature range 300° to 900° K. were made with spectroscopically pure copper rod and with pure silica glass. Heat contents were within 1% of the currently accepted values (*4*).

RESULTS AND DISCUSSION

The measured heat contents for the three crystalline lead silicate compounds are given in Table I. This table also contains the heat contents of glassy ortho and meta lead silicates. The heat content ($H_T - H_{298.15}$) and heat capacity (C_p) equations (*6*) are:

$$H_T - H_{298.15} = aT + bT^2 + cT^{-1} + d \qquad (1)$$

$$C_p = a + 2\,bT - cT^{-2} \qquad (2)$$

for which the values of the constants are given in Table II. To obtain the constants, all the data in Table I were fitted to Equation 1 by regression analysis performed on the IBM 360/50 computer. The average deviation is ±2% for each set of data. One source of error is due to impurities in the compounds (0.5%). Crystallization of the glasses may introduce some uncertainty; however, the effect is not appreciable below 300° C.

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LITERATURE CITED

(1) Bockris, J. O'M., Mellors, G.W., *J. Phys. Chem.* **60**, 1321 (1956).
(2) Dutrizac, J.E., Ph.D. thesis, University of Toronto, Department of Metallurgy and Materials Science, Toronto, Canada, 1967.
(3) Geller, R.F., Creamer, A.S., Bunting, E.N., *J. Res. Nat. Bur. Std.* **13**, 237 (1934).
(4) Kelley, K.K., *U. S. Bur. Mines Bull.* **584**, 1960.
(5) Kubaschewski, O., Evans, E., "Metallurgical Thermochemistry," Academic Press., New York, 1951.
(6) Maier, C.G., Kelley, K.K., *J. Am. Chem. Soc.* **54**, 3243 (1932).
(7) Richardson, F.D., Webb, L.E., *Trans. Inst. Min. Met.* **LXIV**, 529 (1954-55).
(8) Skeaff, J.M., M.Sc. thesis, Department of Metallurgy and Materials Science, University of Toronto, Toronto, Canada, 1966.
(9) Southard, J.C., *J. Am. Chem. Soc.* **63**, 3142 (1941).

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