Reactions 13 and 14 have been indicated as slow, rate controlling reactions in which the proton concentration of solution is of primary importance. It is postulated for mixtures initially rich in DES that the proton concentration is radically decreased over that for mixtures with high initial acid concentration. This hypothesis seems reasonable, since the acidic nature of the $C_2H_5SO_4H$ formed from H_2SO_4 during Reaction 3 would tend to keep the proton concentration constant throughout Reaction 3. This constant proton concentration throughout the reaction coupled with a very great decrease in proton concentration with increase in DES concentration can explain the constancy of k_{F_3} and k_{R_3} for each individual reaction and yet their large variation with initial H_2SO_4 concentration

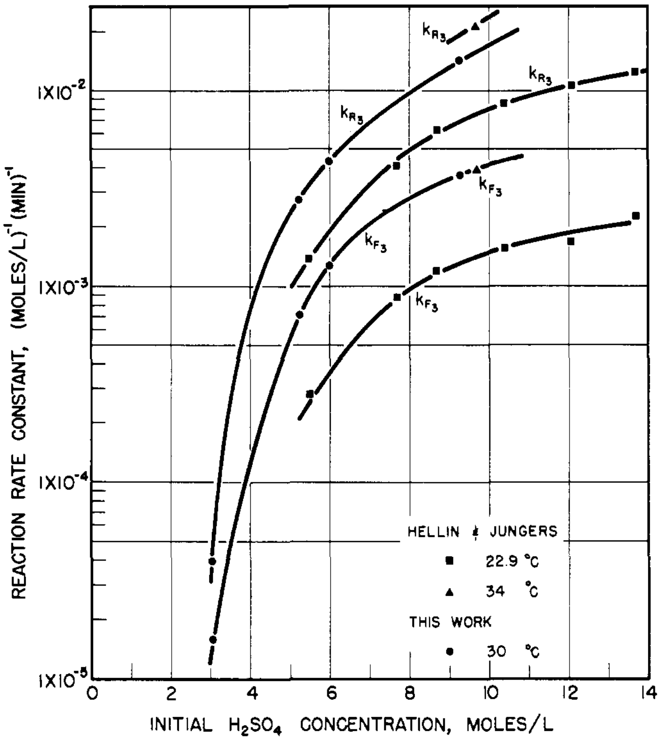

Figure 2. Rate constants for the $C_2H_5SO_4H-(C_2H_5)_2SO_4-H_2SO_4$ reaction as functions of initial H_2SO_4 concentration

LITERATURE CITED

(1) Alexander, E.R., "Principles of Ionic Organic Reactions," Wiley, New York, 1950.
(2) Box, G.E.P., *Bull. Inst. de Statistique* **30**, 215 (1958).
(3) Box, G.E.P., Statistical Technical Research Group, *Rept. No.* 1, Princeton Statistical Center, October, 1957.
(4) Box, G.E.P., Goutie, G.A., *Proceed. Inst. Elect. Eng. (London)* **103B**, *Supl.* 1, 100 (1956).
(5) Brooks, B.T., "The Chemistry of the Nonbenzoid Hydrocarbons," Reinhold, New York, 1950.
(6) Ellis, C., "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.
(7) Harris, H.G., M.S. Thesis, University of Texas, 1962.
(8) Harris, H.G., Himmelblau, D.M., *Anal. Chem.* **33**, 1764 (1961).
(9) Hellin, M., Jungers, J.C., *Bull. soc. chim. France* **1957**, p. 386.
(10) Nemstov, M.S., *Khim. Prom. No.* 8, 15 (1960).
(11) Suter, C.M., "The Organic Chemistry of Sulfur," Wiley, New York, 1944.

RECEIVED for review November 12, 1962. Accepted June 17, 1963 This research was supported by a grant from The Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund.

Thermodynamic Properties of Solid Monoxides, Monosulfides, Monoselenides, and Monotellurides of Ge, Sn, and Pb

CHIKARA HIRAYAMA
Westinghouse Research Laboratories, Pittsburgh, Pa.

The thermodynamic properties of the oxides, sulfides, selenides, and tellurides of Ge, Sn, and Pb are systematically compiled. A number of these values are computed from the most recent published data.

A NUMBER of binary compounds formed between elements of Groups IVA (Ge, Sn, Pb) and VIA (S, Se, Te) of the periodic table are known to be useful semiconducting and photoconducting materials. Recent measurements on the volatility characteristics of sulfides, selenides, and tellurides of this group of compounds make it possible to compute all of the thermodynamic properties of these binary solids with some degree of accuracy. Because of their high dissociation energies these compounds exist in the vapor phase predominantly as the molecular species.

The new reliable data concerning vapor pressures and dissociation energies allow the systematic compilation of thermodynamic data for the IVA-VIA binary compounds. A number of values, such as the heat of formation of SnSe and GeS are reported here for the first time. The thermodynamic properties of these compounds are of interest to solid state physicists as well as to chemists.

RESULTS

The standard heat of formation and entropies of most of the compounds have been tabulated (*15, 18, 27*). Although the vapor pressures of all of the compounds have been reported, the heats of sublimation at 298° K. have not been reported in many cases. Since the high temperature heat capacities of most of these compounds are not available, we have made reasonable estimates in computing the heat of sublimation at 298° K. by the third law method. The high temperature entropy and enthalpy functions of Kelley (*14*) were used.

Table I summarizes the reliable vapor pressures of the solids, with the vapor pressure, in atmospheres, expressed as $\log p = A/T + B$, where A and B are constants, and T is the absolute temperature. The temperature range, in ° C., for each set of measurements is also recorded.

Table II records the entropies of the gaseous species taken from Kelley and King (*15*), and the dissociation energies are taken from dependable sources.

Table III summarizes the thermodynamic data of the the solid compounds. The probable deviations are recorded wherever this information is available with some confidence. The melting points recorded are obtained for the most part from Hansen (*8*) and from Kubaschewski and Evans (*18*). The detailed computation for each compound follows.

GeO. Dennis and Hulse (*6*) reported the preparation of a crystalline black solid which was believed to be GeO. They noted its volatility in nitrogen at 710°, and the ready oxidation of this material when exposed to air. More recently, Bues and Wartenberg (*3*) reported the vapor pressure for the reaction GeO(s) = GeO(g). However, Jolly and Latimer (*13*) have conclusively shown that Bues and Wartenberg had actually measured the vapor pressure over a mixture of Ge and GeO_2. Jolly and Latimer have found that solid GeO is unstable at all temperatures below 600°.

GeS. A number of workers (*1, 16, 29, 30, 34*) in recent years have measured the vapor pressure of GeS with fairly good agreement. The only large disagreement is that reported by Kenworthy, Starliper and Ollar, whose values appear to be too high. The heats of sublimation at 298° K. are computed by the third law method by using the heat capacity of SnO and the vapor pressure reported by the various authors. The heats of sublimation are recorded in Table I; the average value is 39.8 kcal./mole. Barrow, Dodsworth, and Drummond (*1*) previously reported a value of 39.6 kcal./mole which appears high in view of the high heat capacity assumed by these authors.

The heat of formation, ΔH_f°, is calculated by using the dissociation energy (130 kcal./mole) given by Gaydon (*7*), the heats of sublimation of Ge (91.5 kcal./gram atom) and sulfur (56.9 kcal./gram atom) given by Stull and Sinke (*33*), and the heat of sublimation of GeS. The value obtained by the thermochemical cycle is $\Delta H_f^\circ = -21.4$ kcal./mole. The entropy of formation of GeS(s) is $\Delta S_f^\circ = 1.0$ e.u. From the entropies of Ge(s) and S(s) (*33*) the entropy of GeS at 298° K. is 16.0 e.u., and the free energy of formation ΔF_f° is −21.7 kcal./mole. Dennis and Hulse (*6*) report a melting point of 625° for this compound.

GeSe. The vapor pressure of GeSe has been recently measured by Chen-Hwa, Pashinkin, and Novoselova (*4*). Using their data and the heat capacity of SnS the heat of sublimation at 298° K., $\Delta H_s = 45.6$ kcal./mole. From the dissociation energy of 115 kcal./mole (*7*) and the heats of sublimation (*33*) of Ge and Se (49.4 kcal./gram atom), the heat of formation at 298° K. is $\Delta H_f^\circ = -20.1$ kcal./mole. The entropy of GeSe at 298° K. is 18.9 e.u.

GeTe. The vapor pressure of GeTe has been reported by Chen-Hwa, Pashinkin, and Novoselova (*4*), and by Hirayama (*9*). The former workers reported slightly higher vapor pressures than the latter. As a best estimate, the heat capacity of SnS was used to calculate the heat of sublimation at 298° K. from both groups of data. The values obtained are 47.0 and 49.0 kcal./mole, respectively, with an average $\Delta H_s = 48.0$ kcal./mole. From the dissociation energy of GeTe and the heats of sublimation of Ge and Te (19.8 kcal./gram atom (*33*), the heat of formation of GeTe(s) in $\Delta H_f^\circ = -8.0$ kcal./mole. The entropy of formation is 0.6 e.u., the free energy of formation is $\Delta F_f^\circ = -8.2$ kcal./mole, and the entropy at 298° K. is S° = 19.9 e.u.

SnO. Tin monoxide has an incongruent melting point (*31*) of 1040°, and is unstable at temperatures higher than 400°. Humphrey and O'Brien (*12*) have determined the heat of formation, $\Delta H_f^\circ = -68.4 \pm 0.3$ kcal./mole, of SnO from the heat of combustion of tin. The entropy of this compound is reported to be 13.5 ± 0.3 e.u. The entropy and free energy of formation are therefore −23.3 e.u. and −61.5 kcal./mole, respectively. Although SnO partially decomposes to Sn and SnO_2 on heating, the heat of sublimation may be computed from the thermochemical cycle by using the heat of dissociation of SnO (127 kcal./mole) and of oxygen given by Gaydon (*7*), the heat of sublimation of tin (72 kcal./gram atom) (*33*), and the heat of formation. The heat of sublimation of SnO at 298° K. is thus $\Delta H_s = 72$ kcal./mole. The SnO in the gas phase is highly stable against dissociation as noted from the high dissociation energy. Although Spandau and Ullrich (*32*) reported the vapor pressure of SnO between 670° and 1320°, with a heat of sublimation of 38.5 kcal./mole, the values are in great doubt.

Table I. Vapor Pressures of Solid Ge, Sn, and Pb Binary Compounds, $\log P_{atm.} = A/T + B$, and Heats of Sublimation at 298° K.

	$-A$	B	Range, ° C.	Ref.	$\Delta H_{s_{298}}$
Ges	8848	8.834	348–376	1	37.0
	9591	9.476	338–399	29	41.6
	7579	7.17	525–615	30	40.1
	6966	6.215	433–596	34	40.4
GeSe	9384	7.847	414–596	4	45.6
GeTe	10255	8.255	407–564	9	49.0
	10058	8.433	437–606	4	47.0
SnS	10470	7.080	677–802	26	52.6
	10470	7.080	617–811	2	52.8
	9980	6.670	816–880	17	
SnSe	10495	7.318	500–625	10	51.3
	9187	5.815	589–647	23	51.1
SnTe	11211	7.672	519–660	10	53.1
	9817	6.128	575–731	23	52.3
PbO	13320	7.834	614–770	22	64.5
PbS	11780	7.448	775–920	34	56.7
	11672	7.6	825–1025	21	
PbSe	11032	7.203	501–688	35	54.0
PbTe	11636	7.946	511–688	24	53.5

Table II. Entropies and Dissociation Energies of Gaseous Species

	Entropy, S°_{298}, Cal./Mole/Deg.	Dissocn. Energy, D, Kcal./Mole	Ref.
GeO	54.0 ± 0.2	150	(*7*)
GeS	56.3 ± 0.5	130	(*7*)
GeSe	59.2 ± 0.5	115	(*7*)
GeTe	61.1 ± 0.6	94	(*7*)
SnO	55.46 ± 0.10	127	(*7*)
SnS	57.9 ± 0.2	111 ± 3	(*5*)
SnSe	60.8 ± 0.5	86 ± 2	(*10*)
SnTe	62.7 ± 0.5	80 ± 2	(*10*)
PbO	57.34 ± 0.10	99.1	(*25*)
PbS	60.24 ± 0.10	76.1	(*25*)
PbSe	63.0 ± 1.0	61.5 ± 2.5	(*25*)
PbTe	64.9 ± 0.5	51.4 ± 2.0	(*25*)

SnS. The vapor pressure of SnS has been measured with excellent agreement by Richards (*26*) between 677° and 802°, and by Benuni and Tseidler (*2*) between 617° and 811°. Klushin and Chernykh (*17*) extended these measurements to the liquid state with excellent agreement. More recently, Colin and Drowart (*5*) made a mass spectroscopic study of SnS, and obtained a heat of sublimation of $\Delta H_s = 52.6 \pm 1.6$ kcal./mole, in agreement with the data of Richards and of Benuni and Tseidler. The dissociation energy obtained by the former workers is 111 ± 3 kcal./mole; Gaydon (*7*) had previously reported an estimated value of 69.5 kcal./mole. The standard entropy and heat of formation of SnS, determined by Humphrey and O'Brien (*12*), are 18.4 ± 0.2 e.u. and −25.1 ± 1.2 kcal./mole, respectively.

SnSe. The vapor pressure of SnSe has recently been measured by Hirayama, Ichikawa, and DeRoo (*10*) between 500° and 625°, while Nesterova, Pashinkin and Novoselova (*23*) measured it between 589° and 647°. Although the slopes of the vapor pressure curves of these workers deviate (Table I), the vapor pressures measured in the lower temperature region by Nesterova agree with the values in the higher temperature region of Hirayama. The heat of sublimation at 298° K. calculated by the latter workers is 51.3 ± 2 kcal./mole, while the third law calculation from the data of Nesterova yields a value of 51.1 kcal./mole. The heat of formation of this compound is reported (*18*) as −16.5 ± 2 kcal./mole. Using Stull and Sinke's values (*33*) for the heats of sublimation of Sn and Se, the dissociation energy of SnSe is calculated to be 86 ± 2 kcal./mole. Gaydon previously estimated a value of 69 kcal./mole. The entropy of formation is thus 0.1 e.u., and the standard entropy os SnSe is 22.5 e.u., as compared to the estimated value of 20.6 e.u., reported in the Landolt-Börnstein Tabellen (*19*).

SnTe. The heat of formation of SnTe has been measured by McAteer and Seltz (*20*) to be −14.6 kcal./mole. They also calculated a standard entropy of 24.1 e.u. The vapor pressure of this compound was recently measured by Hirayama, Ichikawa, and DeRoo (*10*) between 519° and 660°, while Nesterova, Parshinkin, and Novoselova (*23*) measured it between 575° and 731°. The slopes of the vapor pressure curves of these two workers deviate, but the vapor pressures determined by both groups at overlapping temperatures agree quite well. The heat of sublimation at 298° K. calculated by Hirayama is ΔH_s = 53.1 kcal./mole. Nesterova's data yield a value of 52.3 kcal./mole. The dissociation energy calculated from these data is 80 ± 2 kcal./mole, which differs considerably from Gaydon's estimate of 69 kcal./mole.

PbO. The heat of formation of PbO (yellow) is −52.07 kcal./mole (*27*), and the standard entropy is 16.1 e.u. (*15*). The heat of sublimation at 298° K., based on the recent vapor pressure data of Nesmeyanov, Firsova, and Isakova (*22*), and the heat capacity of Kelley (*14*), is ΔH_s = 64.5 kcal./mole. The dissociation energy has recently been re-evaluated by Porter (*25*) to be 99.1 kcal./mole.

PbS. The heat of formation (*18*) and the entropy of PbS are −22.5 ± 1 kcal./mole and 21.8 ± 0.3 e.u., respectively. The vapor pressure of this compound was measured by Hsiao and Schlecten (*11*) and by Sudo (*34*). The former's vapor pressures, measured by Langmuir method, are about an order of magnitude lower, and are in some doubt. The heat of sublimation at 298° K. calculated from Sudo's data, is 57.7 kcal./mole. Colin and Drowart (*5*) obtained a value of 55.7 ± 0.6 kcal./mole from mass spectroscopic data. The mean value is 56.7 ± 2 kcal./mole. The heat of dissociation (*25*) is 76.1 kcal./mole.

PbSe. The heat of formation (*18*) and entropy (*15*) of PbSe are −18.0 ± 2 kcal./mole and 24.5 ± 0.5 e.u., respectively; the dissociation energy (*25*) is 61.5 ± 2.5 kcal./mole. The vapor pressure has recently been measured by Zlomanov, Popovkin, and Novoselova (*35*). Since high temperature heat capcity data are not available for this compound, we use the heat capacity of PbS to calculate the heat of sublimation at 298° K., ΔH_s = 54.0 kcal./mole.

PbTe. The heat of formation (*18*) and entropy (*15*) are −16.6 ± 0.5 kcal./mole and 26.3 ± 0.5 e.u., respectively; the dissociation energy (*25*) is 51.4 ± 2 kcal./mole. The vapor pressure has been determined by Pashinkin and Novoselova (*24*). We calculate the heat of sublimation at 298° K., ΔH_s = 53.5 kcal./mole, from the vapor pressure data and by taking the sum of the heat capacities of Pb and Te (*14*), taking only the first power terms—$C_p = 9.86 + 8.0 \times 10^{-3}\,T$.

DISCUSSION

In view of the approximations made in the heat capacities of some of the compounds where data are not available, the calculated values in Table III no doubt contain some corresponding uncertainties in the heat of sublimation. However, the error introduced by these approximations should not exceed 2 kcal./mole in each case.

The entropy of formation of the compounds from the solid elements is 0 ± 1.5 e.u., whereas that for the oxides is approximately 24 e.u. Searcy (*28*) recently commented on the significance of the entropies of formation of solid-solid and solid-gas reactions. Because the uncertainties in the calculated values have a greater relative effect on the entropy of formation, any consistent trend in the entropies for the entire group of compounds is not discernible. However, the relative stabilities of any group of chalcogenides of a given metal are clearly indicated in the decreasing negative heats of free energies of formation.

The heat of sublimation of the heavier lead compound is higher than that of the corresponding tin and germanium compounds, where this value is obtained from measured vapor pressures; the exception being SnO which has a calculated heat of sublimation of 72 kcal./mole.

Trends in the vapor pressures in the measured temperature regions are interesting. In the germanium compounds, the vapor pressure increases in the order GeTe < GeSe < Ges, and in the tin series it also increases in the order SnTe < SnSe < SnS; whereas in the lead compounds the order is reversed to PbO < PbS < PbSe < PbTe. There is no apparent trend between the melting point and the vapor pressure.

The IVA-VIA binary compounds show high dissociation energies. Searcy (*28*) states that the dissociation energies of both the gaseous monoxides and dioxides pass through

Table III. Thermodynamic Properties of Solid Ge, Sn, and Pb Compounds at 298° K., and Their Melting Points

			Formation			Heat of Sublim.,
	M.P., ° C.	S°, E.u.	ΔS_f°, e.u.	$-\Delta H_f^\circ$, kcal./mole	$-\Delta F_f^\circ$, kcal./mole	ΔH_s, kcal./mole
GeS	625	16.0	1.0	21.4	21.7	39.8
GeSe	1076	18.9	1.3	19.7	20.1	45.6
GeTe	725	19.9	0.6	8.0	8.2	48.0 ± 2
SnO	1040	13.5 ± 0.3	−23.3	68.4 ± 0.3	61.5	72
SnS	881	18.4 ± 0.2	−1.5	25.1 ± 1.2	24.6	52.7 ± 1.6
SnSe	860	22.5	0.1	16.4 ± 2	16.4	51.2 ± 2
SnTe	790	24.2 ± 1	0.0	14.2 ± 0.3	14.2	52.7 ± 2
PbO	885	16.1 ± 0.2	−23.9	52.1	44.9	64.5
PbS	1119	21.8 ± 0.3	−1.3	22.5 ± 1	22.1	56.7
PbSe	1076	24.5 ± 0.5	−1.1	18.0 ± 2	17.7	54.0
PbTe	917	26.3 ± 0.5	−1.1	16.6 ± 0.5	16.3	53.5

a maximum at main-group and sub-group IV elements. The relationship is probably true for the gaseous sulfides, selenides, and tellurides. There is also a decrease in dissociation energy as the molecular weight increases, as expected.

LITERATURE CITED

(1) Barrow, R.F., Dodsworth, P.G., Drummond, G., Jeffries, E.A., *Trans. Faraday Soc.* **51**, 1480 (1955).
(2) Benuni, A.A., Tseidler, A.A., *Sb. Tr. Gos. Nauch. Issled. Inst. Tsvet. Metal.* **1959**, No. 15, 198; *C.A.* **54**, 20727 (1960).
(3) Bues, W., Wartenberg, H.V., *Z. anorg. allgem. Chem.* **266**, 281 (1951).
(4) Chen-Hwa, Lo, Pashinkin, A.S., Novoselova, A.V., *Zhur. Neorg. Khim.* **7**, 963 (1962).
(5) Colin, R., Drowart, J., *J. Chem. Phys.* **37**, 1120 (1962).
(6) Dennis, L.M., Hulse, R.E., *J. Am. Chem. Soc.* **52**, 3553 (1930).
(7) Gaydon, A.G., "Dissociation Energies and Spectra of Diatomic Molecules," 2nd. ed., Chapman and Hall, Ltd., London, 1953.
(8) Hansen, M., "Constitution of Binary Alloys," 2nd ed., McGraw-Hill, New York, 1958.
(9) Hirayama, C., *J. Phys. Chem.* **66**, 1563 (1962).
(10) Hirayama, C., Ichikawa, Y., DeRoo, A.M., *Ibid.*, **67**, 1039 (1963).
(11) Hsiao, C.M., Schlechten, A.W., *Trans. AIME* **194**, 65 (1952).
(12) Humphrey, G.L., O'Brien, C.J., *J. Am. Chem. Soc.* **75**, 2805 (1953).
(13) Jolly, W.L., Latimer, W.M., *Ibid.*, **74**, 5757 (1952).
(14) Kelley, K.K., "Contributions to the Data on Theoretical Metallurgy," U. S. Bureau of Mines, Bull. No. **584**, 1960.
(15) Kelley, K.K., King, E.G., "Contributions to the Data on Theoretical Metallurgy," U. S. Bureau of Mines, Bull. No. **592**, 1961.
(16) Kenworthy, H., Starliper, A.G., Ollar, A., *J. Metals* **8**, 69 (1956).
(17) Klushin, D.N., Chernykh, V.Ya, *Zhur. Neorg. Khim.* **5**, 685 (1960), (English translation by Chem. Soc. London).
(18) Kubaschewski, O., Evans, E. Ll., "Metallurgical Thermochemistry," 2nd ed., Pergamon Press, London, 1955.
(19) Landolt-Börnstein Tabellen, Sechste Auflage, Band II, Eigenschaften der Materie in ihren Aggregatzustanden, Teil 4, Kalorische Zustandgrossen, 1961.
(20) McAtter, J.H., Seltz, H., *J. Am. Chem. Soc.* **58**, 2081, (1936).
(21) Miller, O.G., Abdeev, M.A., *Tr. Altaisk. Gorno-Met. Nauchn. Issle. Inst. Akad. Nauk Kaz. S.S.R.* **7**, 182 (1958); *C.A.* **54**, 4297 (1960).
(22) Nesmeyanov, A.N., Firsova, L.P., Isakova, E.P., *Zhur. Fiz. Khim.* **34**, 573 (1960) (English translation).
(23) Nesterova, Ya. M., Pashinkin, A.S., Novoselova, A.V., *Zhur. Neorg. Khim.* **6**, 1031 (1961) (English translation by Chem. Soc. London).
(24) Pashinkin, A.S., Novoselova, A.V., *Ibid.*, **4**, 1229 (1959) (English translation).
(25) Porter, R.F., *J. Chem. Phys.* **34**, 583 (1961).
(26) Richards, A.W., *Trans. Faraday Soc.* **51**, 1193 (1955).
(27) Rossini, F.D., Wagman, D.D., Evans, E.H., Levine, S., Jaffe, I., National Bur. Standards, **Circ. 500**, 1952.
(28) Searcy, A.W., "Progress in Inorganic Chemistry," Cotton, F.A., Ed., Vol. III, p. 49, Interscience, New York, 1962.
(29) Shimazaki, E., Wada, T., *Bull. Chem. Soc. Japan* **29**, 294 (1956).
(30) Spandau, H., Klanberg, F., *Z. anorg. u. allgem. Chem.* **295**, 291 (1958).
(31) Spandau, H., Kohlmeyer, E.J., *Ibid.*, **254**, 65 (1947).
(32) Spandau, H., Ullrich, T., *Ibid.*, **274**, 271 (1953).
(33) Stull, B.R., Sinke, G.C., *Advan. Chem. Ser.*, No. 18 (1956).
(34) Sudo, K., *Sci. Rept. Res. Insts. Tohoku Univ., Ser. A* **12**, 54 (1960).
(35) Zlomanov, V.P., Popovkin, B.A., Novoselova, A.V., *Zhur. Neorg. Khim.* **4**, 1231 (1959) (English translation).

RECEIVED for review April 1, 1963. Accepted August 27, 1963.

The Enthalpy of Formation of Lithium Aluminum Hydride

LUDWIG G. FASOLINO
National Research Corporation, Cambridge 42, Mass.

The following heats of solution have been measured in 4.0N hydrochloric acid:

	ΔH_{298} kcal./mole
$Al(c) + 3HCl(aq.\ 4N) \rightarrow AlCl_3(in\ 4N\ HCl) + \frac{3}{2}\ H_2(g)$	-128.27 ± 0.38
$Li(c) + HCl(aq.\ 4N) \rightarrow LiCl(in\ 4N\ HCl) + \frac{1}{2}\ H_2(g)$	-67.05 ± 0.53
$LiAlH_4(c) + 4HCl(aq.\ 4N) \rightarrow (LiCl + AlCl_3)(in\ 4N\ HCl) + 4\ H_2(g)$	-170.59 ± 1.29

From these data the enthalpy of formation of lithium aluminum hydride was calculated to be −24.67 ± 2.21 kcal./mole.

ACCURATE CALCULATIONS in chemical thermodynamics depend upon the existence of reliable thermochemical information. A literature search has shown that the only reported value for the heat of formation of lithium aluminum hydride was determined by Davis, Mason, and Stegman (*4*). In that work, the heat of reaction of the hydride with $HCl \cdot H_2O$ was measured. Calculations with available data, gave a heat of formation of −24.08 ± 0.35 kcal./mole for the hydride. The auxiliary data used by Davis have since been updated by Evans (*5*), and the Davis value for the heat of formation of lithium aluminum hydride has been changed accordingly. The corrected value is −25.74 ± 0.40 kcal./mole. Other auxiliary data used by Davis are presently being updated by Evans and, therefore, the heat of formation value remains subject to slight change.

The calculation of the enthalpy of formation of lithium aluminum hydride by measuring separately the heats of solution of lithium, aluminum, and lithium aluminum hydride in 4.0*N* hydrochloride acid is described. From the heats of solution data, the enthalpy of formation of the hydride was calculated.

EXPERIMENTAL

Calorimeter. The heats of solution were measured in a modified Parr combustion calorimeter operated adiabatically. The reaction bomb consisted of a nickel alloy body, the inner wall of which was gold-plated. A special bomb